

INFLUENCE OF SOIL ORGANIC MATTER ON PHOSPHORUS AND
OXALATE SORPTION AND DESORPTION IN
A SPODOIC HORIZON

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1995

ACKNOWLEDGMENTS

It is my privilege to express my sincere gratitude, appreciation and heartfelt thanks to Nick B. Comerford, my advisory committee chairman, for his able guidance, keen interest, constructive criticism and constant encouragement during the course of this investigation. I feel pleasure also in expressing high regards to other members of my advisory committee, Earl Stone, Brian McNeal, Cliff Johnston, P. Surash Rao, H. Gholz and Eric Jokela, for my scientific development.

The financial support provided by the National Science Foundation for funding my assistantship and the experimentation is greatly acknowledged. I appreciate also the valuable technical assistance of Mary McLeod, Randy, and Dr. Cliff Johnston at various phases of the work. Mary's friendship was invaluable as was her advice on a wide range of issues. My sincere thanks are also due to everyone in the Forest Soils Laboratory for their cooperative attitude and discussions during the various phases of this investigation. I enjoyed all of my new friendships, especially those of my fellow graduate students.

Finally, I want to thank my wife Gurmeet and my son Kulraj for their patience, love and understanding during this adventure. Without their tolerance and moral support, I would have not done it.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

INFLUENCE OF SOIL ORGANIC MATTER ON PHOSPHORUS AND
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May, 1995

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Major Department: Soil and Water Science

Phosphorus (P) deficiencies are common for poorly-drained Spodosols of the flatwoods region of the Lower Coastal Plain of the Southeastern United States. Large quantities of total P may be present in spodic horizons, but the level of water-soluble P tends to be quite low. The goal of this investigation was to study P and oxalate sorption and desorption by the clay fraction and whole-soil material of a spodic horizon as influenced by soil organic matter. Understanding the sorption mechanisms for P in the presence of oxalate and soil organic matter should form the basis for explaining P extraction by roots from soil surfaces, and the buffering of P levels in soil solutions.

The spodic horizon had a higher capacity to sorb P compared to oxalate,

with soil organic matter significantly reducing the sorption of both P and oxalate. Maximum reduction in P sorption (about 50%) was observed when both organic carbon and oxalate were present in the system. Ligand exchange apparently was the dominant mechanism for P and oxalate sorption. Some of the sorption sites were common for both the anions. Oxalate and P formed different types of surface complexes, with pH determining the type of surface complex formed by oxalate. Oxalate formed monodentate and/or binuclear surface complexes at pH 3.5, while bidentate complexes at pH 4.5 and 5.5. P formed monodentate and/or binuclear surface complexes at pH 4.5.

Significant amounts of organic carbon, Al and Fe were released into solution during the sorption of oxalate. This study provided the first experimental evidence for Stumm's theory of congruent dissolution of minerals by oxalate.

Oxalate desorbed large amounts of P into solution. The presence of organic matter further increased the amount of P desorbed. Oxalate appeared to desorb the P both through ligand exchange and surface dissolution. This could increase the initial P concentration in solution and effect the P buffer power. Since oxalate formed stronger complexes on the mineral surfaces P failed to desorb the oxalate into solution.

CHAPTER 1

GENERAL INTRODUCTION

Phosphorus in Flatwood Spodosols

Phosphorus (P) deficiencies are common for the poorly-drained Spodosols of the flatwoods of the lower Coastal Plain of the Southeastern United States (Comerford *et al.*, 1984). Cycling of P, which occurs through mineralization, immobilization and redistribution of P in soil, depends on its physico-chemical properties. These include P sorption by colloidal surfaces, as well as microbial, mycorrhizal and plant uptake of P (Stewart and Tiessen, 1987). Soil phosphorus can be divided into three general categories: i) ions and compounds in the soil solution, ii) ions sorbed onto or incorporated into the surfaces of inorganic constituents, and iii) ions that are components of soil organic matter.

Inorganic P in the soil solution of a Spodosol's A horizon is replenished by mineralization of organic P, phosphorus leaching from the forest floor, and sometime, by fertilizer application (Polglase *et al.*, 1992). Mineralogy of the surface soil and bleached E horizon is dominated by quartz (Carlisle *et al.*, 1988). Therefore, mineralization of organic matter, plays an important role in P availability. In many of these soils, mineral components have virtually no P retention capacity

in their surface horizons (A and E), either due to low clay contents or the nature of the clay fractions (Ballard and Fiskell, 1974; Fox *et al.*, 1990b; Yuan, 1992). For the surface soils, a clay content as low as 10 g kg⁻¹ is common. Thus P, along with organic matter, can be leached from the surface horizon and accumulate in the underlying spodic horizon.

Spodic Horizons

Organic matter migrates through the A horizon of Spodosols in soluble and colloidal forms and is adsorbed or precipitated, immobilized in the Bh horizon. Current concepts of the formation of spodic horizons are based on the formation of Al and/or Fe humic complexes. Stability and mobility of these compounds depend on the metal concentration in the soil solution. If the amount of Al and/or Fe available for organo-metal complex formation is low in the A horizon, complexes will be formed in the A horizons with low metal/organic ratios. In this case the amount of Al and/or Fe chelated is insufficient to cause immobilization of metal organic compounds, and may then move down in the pedon. During the downward migration, these metal-organic compounds (De Coninck, 1980), concurrently sorbed more polyvalent cations, which results in a progressive decrease of their net negative charge. The presence of higher concentrations of Al and Fe in the subsoil and/or at pH values different from that of the surface horizon may eventually neutralize the remaining charge. This results in the precipitation of metals along with organic matter in subsurface horizons and leads to the

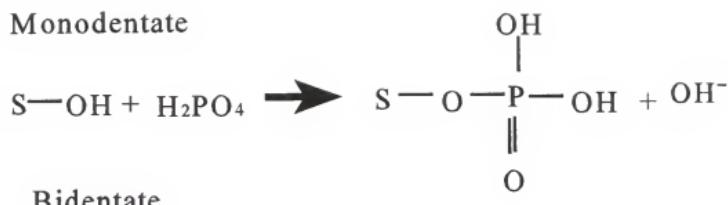
development of a spodic horizon (De Coninck, 1980; Farmer *et al.*, 1983; Buurman, 1984; Tan, 1986; Ugolini *et al.*, 1988). Therefore, the complexation and translocation of Al and Fe by organic acids is a primary mechanism during the podzolization process. This can result in large accumulations of organic carbon (which is mostly as humic and fulvic acid), Al, and Fe in spodic horizons.

Phosphorus in Spodic Horizons

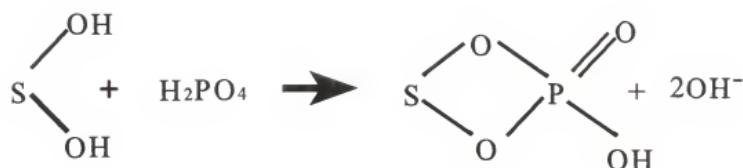
Spodic horizons contain elevated levels of amorphous or poorly crystalline Al oxides, which can sorb P. Not all of this sorbed P is in plant-available form (Ballard and Fiskell, 1974). Large quantities of total P may be present in spodic horizons, but the level of water-soluble P tends to be quite low. The physico-chemical sorption of P is as an inner-sphere complex at the surface of Al and Fe hydroxides and at the broken edges of silicate clay minerals (Sposito, 1984). An inner-sphere P complex refers to a surface complex resulting from ligand exchange between a surface Lewis acid site (S) and the adsorbed ion (Parfitt, 1978; Goldberg and Sposito, 1985). Such complexes are quite stable, showing mainly covalent or ionic bonding character.

Three types of inner-sphere P complexes have been postulated: monodentate, bidentate and binuclear (Fig. 1; Parfitt *et al.*, 1977). Tejedor-Tejedor and Anderson (1990) used fourier transform infrared spectroscopy (FTIR) to study the sorption of orthophosphate onto goethite particles in an aqueous suspension. They observed the formation of three different types of complexes: protonated and

Monodentate



Bidentate



Binuclear

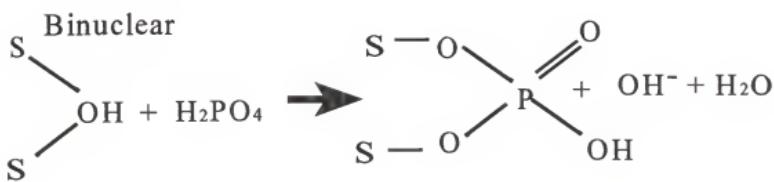


Figure 1.1. Three possible phosphate surface complexes. "S" could represent either Al or Fe.

nonprotonated bidentate bridging, and a nonprotonated monodentate complex. The speciation of these complexes was a function of pH, as pH determines the species of phosphate in solution. They also identified a monodentate complex on the geothite surfaces when the iron/phosphate ratio was less than unity and pH was between 3.5 and 6.0. At higher pH (6.0 to 8.3) and higher concentrations of phosphate in the system, surface complexes were bidentate. Therefore, the type of inner-sphere complex in different soils may be determined by the pH and the concentration of available P in soil solution. Nanzyo (1987) studied sorbed phosphate species using diffuse reflectance infrared spectroscopy (DRIR) and found that phosphate reacts not only with surface sites but also with the structural aluminum of allophanic soils. He reported that P can also precipitate as noncrystalline aluminum phosphate. Most of the studies, however, that have been carried out on the mechanism of P retention and release have used pure Fe & Al oxides as the solid matrix. None of these studies were accomplished using soil materials, where different soil components may coexist.

Organic Anions in Soil

A wide variety of low molecular weight organic anions have been identified in forest and agricultural soils (Stevenson 1982). The commonly found organic anions include oxalate, citrate, formate, acetate, malate, maleate, lactate and fumarate (Gardner *et al.*, 1982; Hue *et al.*, 1986; Pohlman and McColl, 1988). Fox and Comerford (1990) reported that oxalate comprised 60 to 80 percent of

the identified, free, low molecular weight, organic anions in a group of Spodosols from north Florida. They also reported that the oxalate levels in soil solutions averaged an order of magnitude higher in spodic horizons than in the corresponding surface A horizon. These data show that oxalate is present and, if it also affects P sorption, could play a significant role in forest productivity.

Influence of Organic Anions on Phosphorus Availability

Fox *et al.* (1990a) proposed that, in lower Coastal Plain Spodosols, low molecular weight organic anions, whether leached from the surface horizon or produced in situ, might stimulate the release of phosphorus from mineral surfaces. Organic anions acting as ligands are known to release P by i) replacing P sorbed at surfaces of Al or Fe oxides through ligand-exchange reactions (Huang and Schnitzer, 1986); ii) dissolving metal oxide surfaces and releasing sorbed P (Martell *et al.*, 1988); and iii) complexing Al and Fe in solution, thus preventing the re-precipitation of metal-P compounds (Ng Kee and Huang, 1977). It has also been observed that organic anions may block sites on mineral surfaces and reduce P sorption (Kafkafi *et al.*, 1988).

Huang and Violante (1986) studied aluminum-citrate complexes in aqueous solution. They reported that Al and citrate form a 1:1 complex where the citrate ligand occupies three of the six coordination sites around each Al while each of the other three sites are occupied by a water molecule. Occupation of coordination sites by citrate instead of water imposes a restriction on the

subsequent hydrolysis of hydroxy-aluminum polymers. The greater the concentration of organic anions in the system, the greater should be the replacement of water molecules and the blocking of Al coordination sites. Therefore, the occupation of coordination sites by organic ligands would also block sites which would otherwise be available for the sorption of P. Thus, organic anions, through their reactions with Fe and Al both in solution and at soil surfaces should increase the availability of P in soils (Martell *et al.*, 1988). The activity of these surface sites available for coordination with organic ligands, and the activity of ligands in the solution, strongly depend upon pH. The role of pH would be through i) its effect on the relative fractions of various species of organic anions in solution (and these species differ in their affinity for the adsorbent); ii) the variation in charge density of the solid surfaces with pH; and/or iii) competition between OH⁻ and the organic anion for common sorption sites.

Release of P is possible only if the stability of the metal-organic complex is higher than that of the solid-phase metal-P complex. The stability of soluble metal-organic complexes depends on the presence and molecular arrangement of carboxylic and phenolic functional groups on the organic anion (Pohlman and McColl, 1986; Martell *et al.*, 1988). Formation constants can be used to predict the relative effectiveness of different organic acids for releasing P into solution. Organic anions such as oxalate and malate have been classified as having high complexing ability for Al and Fe (Fox *et al.*, 1990b; Pohlman *et al.*, 1990) when they tend to form five- and six-membered rings between the anion and metal.

Therefore, a low molecular weight organic anion like oxalate could play an important role in solubilizing soil Al, therefore indirectly affecting the availability of phosphorus in forest soils.

Among 16 organic anions studied, a threshold value for $\log K_{Al}$ between 4.0 and 4.5 was required before substantial amounts of P were released from a spodic horizon in Florida (Fox *et al.*, 1990a). Beyond this $\log K_{Al}$ value, release of Al and inorganic P increased with increasing formation-constant values.

Violante *et al.* (1991) and Violante and Gianfreda (1993) studied the competitive sorption of phosphate and oxalate on aluminum oxide and montmorillonite. They reported that oxalate and P ions competed strongly for the same adsorption sites on Al oxides under both acidic and neutral conditions. Lan *et al.* (1994) studied the release of P by oxalate from different spodic horizons of different soils. These soils desorbed variable amounts of P, although each contained about the same amount of total P. The differences in P release may have been related to mechanisms by which the P was held by different soil components (crystalline minerals, an amorphous fraction, occluded P, or organo-mineral complexes) and/or the interaction of oxalate with these components.

Oxalate may influence P availability through its reaction with Al both in solution and at the surfaces of Al oxides as it forms stable complexes with Al (Martell *et al.*, 1988). Release of P by oxalate could be by direct ligand exchange and/or dissolution of Al oxide mineral surfaces (Stumm and Morgan, 1981; Huang and Violante, 1986). Stumm (1986) proposed a theory of congruent dissolution of

mineral surfaces by low molecular organic anions. He suggested that organic ligands form complexes with Al and Fe both in solution and on the surfaces of oxides. The formation of complexes in solution by organic ligands increases the rate of dissolution of Al-oxalate complexes on surfaces. Ligand exchange at the surface decreases the strength of Al-OH-Al bonds and helps bring Al-oxalate complexes into solution. This rupture is thought to be induced by the competition of oxalate with the hydroxyls linking the aluminum atoms. Stumm (1986) further proposed that surface complexation is a prerequisite for nucleation for most solid crystals formed in solution as well. However, there is no experimental evidence in the literature to support the above theory, even with the use of pure clay minerals or Al and Fe oxides.

The complexation and sorption reactions of humic and fulvic acids with Al and Fe are similar in magnitude to those for the corresponding monomeric units (e.g. carboxylate, salicylate, dihydroxybenzoate) believed to contain functional groups similar to those in fulvic and humic acid (Stumm and Morgan, 1981; Stevenson and Fitch, 1986; Tan, 1986). Inoue and Wada (1971) concluded that the adsorption of fulvic and humic acids by allophane and imogolite resulted from the ligand exchange of oxygen in carboxylic groups with structural oxygen in the coordination shells of Al and Fe atoms. This suggests that organic carbon may block some of the adsorption sites which might otherwise be available for the sorption of P and organic anions. There are no studies to my knowledge which

examine the influence of natural soil organic carbon on the retention and release of organic anions and P in Spodosols.

A significant portion of the total P in a spodic horizon is inorganic, but not readily available for plant use. Phosphorus uptake by plants is influenced by the amount of root surface area, root growth rate, and P concentration in solution at the root surface (Barber, 1984). Phosphorus supplying capacity of a soil is determined not only by the amount of P in the soil solution but also by the soil's ability to replenish P lost from soil solution and/or during transport of P to plant roots via diffusion and/or mass flow. The soil's ability to replenish P lost from the soil solution depends partially upon release of P from sorbed and insoluble P. Thus, it is important to understand how P is being held by different colloidal surfaces as well as the influence of various chemical processes on the release of previously sorbed and insoluble P.

From the aforementioned, it can be concluded that there is a need to understand how forest trees acquire nutrients from the soil profile in lower Coastal Plains. We can start to address this question by i) understanding the types of sites available and binding mechanisms for oxalate via spectroscopic studies; ii) investigating P sorption and desorption in the presence of oxalate in spodic horizons; and iii) defining the influence of soil organic colloids on the retention and release of P and oxalate. Understanding the sorption mechanisms for P in the presence of oxalate should form the basis for explaining P extraction by roots from soil surfaces, and the buffering of P levels in soil solutions.

CHAPTER 2

INFLUENCE OF SOIL ORGANIC MATTER AND pH ON OXALATE SORPTION ONTO A SPODIC HORIZON

Introduction

Natural organic anions in soils and freshwater environments are derived from plant and animal residues, microbial metabolism and canopy drip. Simple aliphatic anions such as citrate and oxalate are continuously produced through the activities of microorganisms (Flaig, 1971), aqueous extraction of leaves (Bruckert, 1971; Stevenson, 1982), and activities of microorganism and/or roots in the rhizosphere (Reddy *et al.*, 1977). The type of vegetation, pH, oxidation potential, water potential and temperature each affect the kinds and amounts of low molecular weight organic anions that are produced (Stevenson, 1982; Goh and Haung, 1986; Hue *et al.*, 1986; Pohlman and McColl, 1988).

Among the aliphatic anions detected in the extracts of litter and soils, oxalate occupies an important place in many ecosystems, both in well-, and poorly-drained soils (Vedy and Bruckert, 1982). For many organisms, oxalate is a metabolic end product of low residual nutrient energy (Cromack *et al.*, 1979). Smith (1969) and Fox and Comerford (1990) measured significant concentrations of

oxalate (up to 2 mM) and other carboxylic anions in a variety of sediments, in the forest floor, in bulk soil, and in the rhizosphere of forest trees.

Oxalate alters chemical processes in soils through complexation reactions with Al and Fe that occur in the soil solution and on the surfaces of soil particles (Stumm, 1986; Martell *et al.*, 1988). It has acidic characteristics due to the presence of -COOH groups and reacts with mineral soil surfaces through i) electrostatic attractions, ii) complex or chelate formation, and iii) water bridging (Tate and Theng, 1981). Three types of inner-sphere oxalate complexes with soil surfaces are possible: monodentate, bidentate, and binuclear (Parfitt *et al.*, 1977). Each requires the displacement of OH₂ or OH⁻ that had been coordinated to Al and Fe atoms on the surfaces. Such a reaction would increase the pH of the system. Therefore, the amount of OH⁻ released could be used to identify possible reactive sites and possible mechanisms of oxalate sorption at different concentrations of oxalate and/or pH. A change in pH would alter the soil surface charge and, possibly, the species of organic ligand present in the system.

Spodosols of the southeastern Coastal Plain have an accumulation of organic matter in their spodic horizons. As organic anions originate in the forest canopy or forest floor, they form mobile complexes with Fe and Al, and move to the Bh horizon where they are constrained as organo-minerals. Researchers have shown that organic matter may be immobilized through complex interactions with mineral surfaces (Greenland, 1971; Davis and Glour, 1981; Sibanda and Young,

1986). The reactivity of labile soil organic matter is generally attributed to the presence of carboxyl (-COOH) and phenolic hydroxyl (-OH) groups.

The major mechanisms by which soil organic matter is sorbed to mineral surfaces include i) anion exchange, ii) ligand exchange-surface complexation, iii) hydrophobic interaction, iv) hydrogen bonding, and vi) cation bridging (Sposito, 1984). Parfitt *et al.* (1977) suggested that carboxyl groups of fulvic and humic acid replace surface OH⁻ from gibbsite, goethite and imogolite. Ligand exchange of surface-coordinated OH⁻ and OH₂ from Fe oxides by humic substances had also been noted by Tipping (1981b). Jardine *et al.* (1989) suggested that the primary mechanism of dissolved organic carbon sorption is physical adsorption followed by an anion exchange mechanism. This suggests that organic carbon should alter the surfaces charge, surface area and retention properties of inorganic colloids in spodic horizons.

According to Stumm (1986), organic ligands form complexes with Al and Fe in solution and on the surfaces of Fe and Al oxides. The formation of such complexes in solution increases the rate of dissolution of surface complexes.

Huang and Violante (1986), Miller *et al.* (1986), Tan (1986), and Pohlman and McColl (1986) also reported that organic anions which formed complexes with Al and Fe stimulated the dissolution of Al and Fe solid phases. Ohman and Sjoberg (1988) proposed that polycarboxylic acids are effective in solubilization of Al surfaces. They proposed this as a series of complexation-hydrolysis reactions:



where S represents the mineral surface, L is the organic ligand, aq is the solution phase and p, q and r are the number of atoms in each molecule. The calculations of soil solution speciation with kaolinite as the solid phase, showed that, under acidic conditions, solution concentration of Al would increase in the presence of oxalate. This increase was attributed to the formation of $[\text{AlL}]^+$ and $[\text{AlL}_2]^-$ species in solution. Fox *et al.* (1990a) observed higher release of Al into solution with the adsorption of oxalate, and attributed this to the dissolution of solid-phase Al surfaces in Spodosols. Bilinski *et al.* (1986) found that the binuclear complex $\text{Al}_2(\text{OH})_2(\text{C}_2\text{O}_4)_4^{4-}$ formed in solution when oxalate concentration was high, and then precipitated as Al oxalate with the oxalate ion acting as a bridging ligand between two aluminum atoms.

The objectives of the present study were to describe i) oxalate sorption on the clay fraction of a spodic horizon, ii) the effect of soil pH on oxalate sorption capacity, and iii) the influence of soil organic matter on oxalate sorption using fourier transform infrared (FTIR) spectroscopy.

Materials and Methods

Soil Material

Soil was collected from the spodic horizon (Bh) in a soil pit of a Pomona series (sandy, siliceous, hyperthermic Ultic Alaquod) at the Gator Nationals Forest site located in Alachua County, 10 km northeast of Gainesville, Florida (Swindel *et*

al., 1988). The soil material was air dried, passed through a 2-mm sieve and stored in plastic bags.

Preparation of Whole Soil

Two sets of soil samples were prepared: one with organic matter and the other without organic matter. One portion was treated with hot, 30% H_2O_2 to remove organic matter as outlined by Kunze and Dixon (1986). This sample was centrifuged and washed several times with distilled water, while the other portion was not treated. Both soil samples (with and without organic matter) then were saturated with Na using 0.01 M NaCl. Excess Na was removed with four or five centrifugal washings using distilled water. The samples were oven dried at 110 °C.

Preparation of the Soil Clay Fraction

The water-dispersible clay fraction was separated by ultrasonification at a 1:5 soil to water ratio (Genrich and Bremner, 1974). After ultrasonification, wet-sieving was used to remove the sands. The clay fraction (< 0.2 μm diameter) was separated by centrifugal sedimentation (Jackson, 1979). The resulting clay was divided into two portions. One portion was treated with hot, 30 % H_2O_2 to remove organic matter as outlined by Kunze and Dixon (1986). The other portion was not treated. Both clay samples (with and without organic matter) then were

saturated with Na using 0.01 M NaCl. Excess Na was removed with four or five washings using distilled water. The samples were oven dried at 110 °C.

Mineralogy of the Clay Fraction

Mineralogy of the clay was determined by X-ray diffraction (XRD) on parallel-oriented specimens, using Cu-K α radiation. Approximately 250 mg of clay were deposited on a ceramic tile under suction followed by K and Mg saturations on the tiles by washing with the respective chloride salt and rinsing. Glycerol then was added to the Mg saturated samples. Samples were scanned at 2° 2θ per minute, at 25 °C for both the K- and Mg-saturated samples. Minerals were identified from XRD peak positions, making use of differentiating responses to ion saturation. Detectable minerals in the clay sample included quartz, kaolinite, hydroxy interlayered vermiculite, and gibbsite.

Oxalate Sorption Studies

Sorption experiments were carried out with different concentrations of oxalate over a pH range (3.5, 4.5 and 5.5). Triplicate samples of clay (250 mg with and without organic matter) were placed in 30 ml bottles with 25 ml of solution having an oxalate concentration of 0 mM, 0.1 mM, 1.0 mM, or 10 mM adjusted initially to pH 3.5, 4.5 or 5.5 (using 0.1 M HCl or NaOH). Triplicate five-gram whole-soil samples from each treatment (with or without organic matter) were placed in 100 ml bottles with 50 ml of solution having an oxalate

concentrations of 0 mM, 0.1 mM, 0.5 mM, 1.0 mM, 3.0 mM, 7.0 mM or 10 mM adjusted initially to pH 4.5 (using 0.1 M HCl or NaOH).

Two drops of toluene were added to inhibit microbial growth and all samples were placed in a reciprocating shaker for 24 hrs. The pH of the suspension was periodically (every three hours) adjusted with 0.1 M HCl or NaOH over the 24 hrs of the experiment, to maintain the initial pH. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. The adsorbate was used for FTIR analysis and the filtrate was analyzed for oxalate, Al, Fe, and organic carbon. Sorbed oxalate was calculated from the difference between the initial and final oxalate concentration in solution.

Chemical Analysis

Solution pH was measured using a combination glass electrode and an Orion pH meter. Aluminum was determined via flame emission spectrophotometer with a N₂O-C₂H₂ flame. Fe was also determined, with an acetylene flame. Total organic carbon content of the clay suspension (with organic matter) was measured via persulfate oxidation and IR analysis of CO₂ produced on a TOC apparatus (College Station TX). The E4 ($\lambda=465$) to E6 ($\lambda=665$) ratio of organic carbon released in solution by clay with organic matter was measured using a Shimadzu UV/Vis spectrophotometer.

Oxalate in the extract was determined by HPLC (Fox and Comerford, 1990a) using a Hamilton PRP-X300 150 x 4.1 mm organic acid column (Hamilton

Co., Reno, Nevada) with a Gilson single piston high pressure pump along with a Pheodyne model 7125 injection valve fitted with a 20 μL injection loop. The HPLC system used a Gilson Holochrom variable wavelength UV detector in conjunction with a Gilson computerized integrator. The eluent was 0.005 M H_2SO_4 at a flow rate of 2 mL min^{-1} . Oxalate concentration was calculated from the calibration curve obtained with standard solutions of 0.1 to 10 mM.

Titration Curves for the Clay Fractions and the Whole Soil Material

To determine the amount of OH released into solution during the sorption of oxalate, titration curves were prepared (Duquette and Hendershot, 1993) for each of the clay and whole-soil samples (i. e., with and without organic matter). Duplicate one-gram samples of clay and 10-gram samples of soil were equilibrated with 100 mL of water adjusted to pH 3.0. The suspension was allowed to equilibrate for 24 hrs. Titration was carried out with 0.1 N NaOH from pH 3.0 to 7.0. With each addition of 0.1 ml NaOH, the solution was allowed to equilibrate for 2 to 5 minutes or until pH stabilized. The titration curves, for each type of clay and soil are presented in Appendix A-1 and Appendix A-3. pH buffer curves were calculated which relate the change in pH with unit additions of NaOH for three different ranges of pH. These ranges were 3.44 to 4.44, 4.44 to 5.65, and 5.45 to 6.75. Models were fit to these curves and used to calculate the change in OH concentration required to change pH of the system to specific values (Appendix A-2 and Appendix A-4).

FTIR Analysis

FTIR spectra were obtained by placing small amounts of clay suspension on AgCl windows and allowing the deposit to dry. Spectra then were collected on a Bomem DA3.10 spectrophotometer equipped with a MCT detector and a KBr beam splitter, operating at 2.0 cm^{-1} resolution. The Bomem DA3.10 spectrophotometer was controlled through a general-purpose interface bus (IEEE-488) interfaced to a DEC Vaxstation-II computer.

Adsorption Isotherms

The Langmuir adsorption model was fitted to all sorption data. The following equation was used:

$$S = \frac{S_m KC}{1 + KC} \quad (2.2)$$

Where S is the amount of oxalate taken up per unit mass of soil (mM kg^{-1}), S_m is the maximum amount of oxalate that was bound, C is the equilibrium concentration of oxalate (mM), and K is a constant related to the binding energy for oxalate. The parameters (K and S_m) were calculated by a least squares fit to a linear form of the equation:

$$\frac{C}{S} = \frac{1}{KS_m} + \frac{C}{S_m} \quad (2.3)$$

Speciation Calculations

The metals speciation model MINTEQA2 version 3.2 was used to calculate the species of Al and oxalate in solution, assuming that the system was under equilibrium conditions. Calculations were carried out at solution concentrations of oxalate and Al for the highest loading rate of oxalate (10^{-2} M oxalate) at different pH values. Log K values for soluble Al-oxalate complexes were obtained from Thomas *et al.* (1991). Log K was assumed to be 6.12 for AlC_2O_4^+ and 11.15 for $\text{Al}(\text{C}_2\text{O}_4)_2^-$. Two solid phase species of Al-oxalate were considered in the speciation model. The formation constants were taken from Bilinski *et al.* 1986. The values of constants used were 21.87 for $\text{Al}_3(\text{OH})_7(\text{C}_2\text{O}_4)_3\text{H}_2\text{O}$ and 5.61 for $\text{NaAl}(\text{OH})_2(\text{C}_2\text{O}_4)_3\text{H}_2\text{O}$. Formation constants used for calculations of other species were those of the MINTEQA2 data base taken from Martell and Smith (1982).

Statistical Analysis

Statistical differences between different regression lines at each pH value were tested using the General Linear Models procedure of the SAS framework (SAS Institute, 1985). The model used was:

$$Y_{ij} = \alpha + \beta X_{ij} + \epsilon_{ij} \quad (2.4)$$

where α is the intercept, β is slope of the line, and ϵ is the error term. To compare two regression lines, we compared the α and β values of the respective

lines. The ANOVA and t tests were used to test the differences between α_1 and α_2 as well as between β_1 and β_2 . Significance of the difference between means was determined by the t-test (Snedecor and Cochran, 1980). Standard deviations or standard errors of means are given as well, when appropriate.

Results

Characterization of the Clay Fraction using FTIR

FTIR spectra of clay samples with and without organic matter are presented in Figure 2.1. Characteristic infrared bands for quartz, kaolinite, HIV and gibbsite minerals are identified. The broad OH-stretching band in the region 3000 to 3600 cm^{-1} , along with well defined OH-stretching is characteristic of kaolinite, HIV and gibbsite, while the broad deformation band for water in the 1640 cm^{-1} region suggests the presence of amorphous clay. The spectra of clay with organic matter shows major absorption bands as well in the regions of 3300 cm^{-1} (O-H and N-H stretching), 2960/2925 cm^{-1} (aliphatic C-H stretching of CH_3 and $-\text{CH}_2$ groups), 1610 cm^{-1} (aromatic C=C and/or H-bonded C=O stretching of COOH), and 1400 (OH deformation, C-O stretching of phenolic OH, and C-H deformations of CH_3 and CH_2) together with the characteristic infrared bands for quartz, kaolinite, HIV and gibbsite minerals. Intensity of the broad OH-stretching band in the region 2700 to 3600 cm^{-1} for clay with organic matter was greater, reflecting the presence of OH-stretching associated with organic matter.

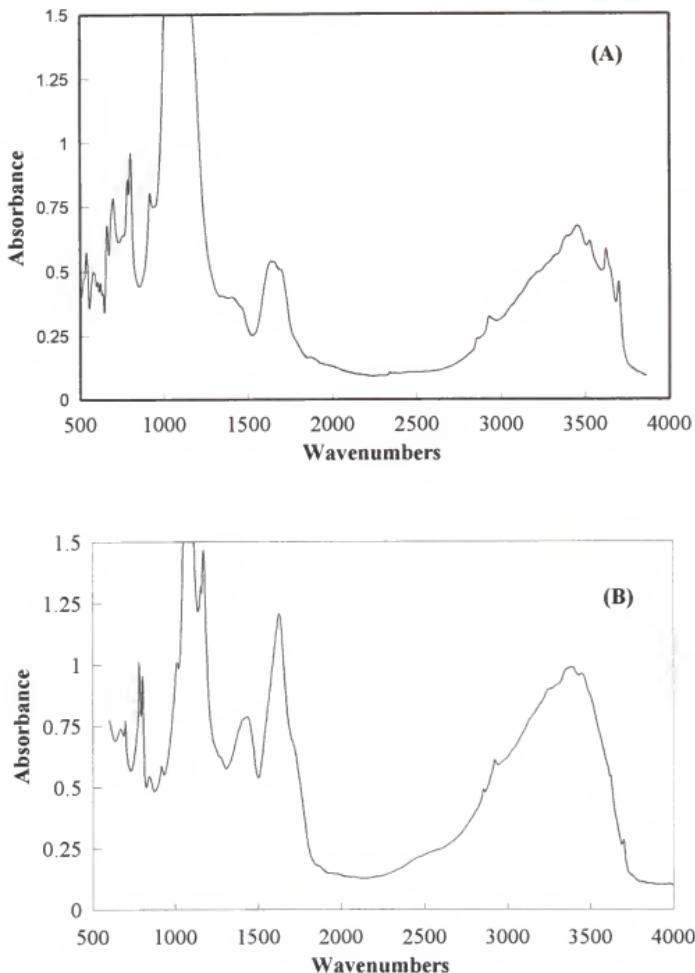


Fig. 2.1 FTIR spectra of clay (a) without organic matter and (b) with organic matter.

Sorption of Oxalate by the Clay Fractions

Sorption isotherms for oxalate on clay samples with organic matter and without organic matter at constant pH are presented in Figure 2.2. Linear isotherms provided best fit for the data within the range of oxalate concentrations used. Parameters of the model at different pH values are presented in Table 2.1, with oxalate sorption being strongly dependent on pH. As pH increased, the oxalate sorption decreased. Soil organic carbon also had a significant influence on oxalate sorption at all pH values, with approximately a 2 to 3 fold reduction in oxalate sorption in the presence of organic carbon (Table 2.1).

FTIR spectra at the highest oxalate loading are presented in Figure 2.3 for clay without organic matter and in Figures 2.4, 2.5, and 2.6 for clay with organic matter. A small shoulder was seen at 1710 cm^{-1} for the FTIR spectra of clay with organic matter for the 10^{-2} M oxalate loading at both pH 3.5 and 4.5. Parfitt *et al.* (1977) also observed the same bands for oxalate sorption by goethite and proposed the formation of a binuclear complex between oxalate and two Fe^{3+} ions. If inner-sphere complexes form between oxalate and clay surfaces, they must involve the coordination of carboxylic groups from the oxalate ion with Al and/or Fe atoms of the clay surface, through oxygen atoms. However, the absorption bands linking Al-oxalate vibrations, which would normally provide the most direct information on complexation, are too weak to be definitive. It was not possible to isolate these bands from the FTIR spectra of the clay due to the low surface concentrations of the oxalate.

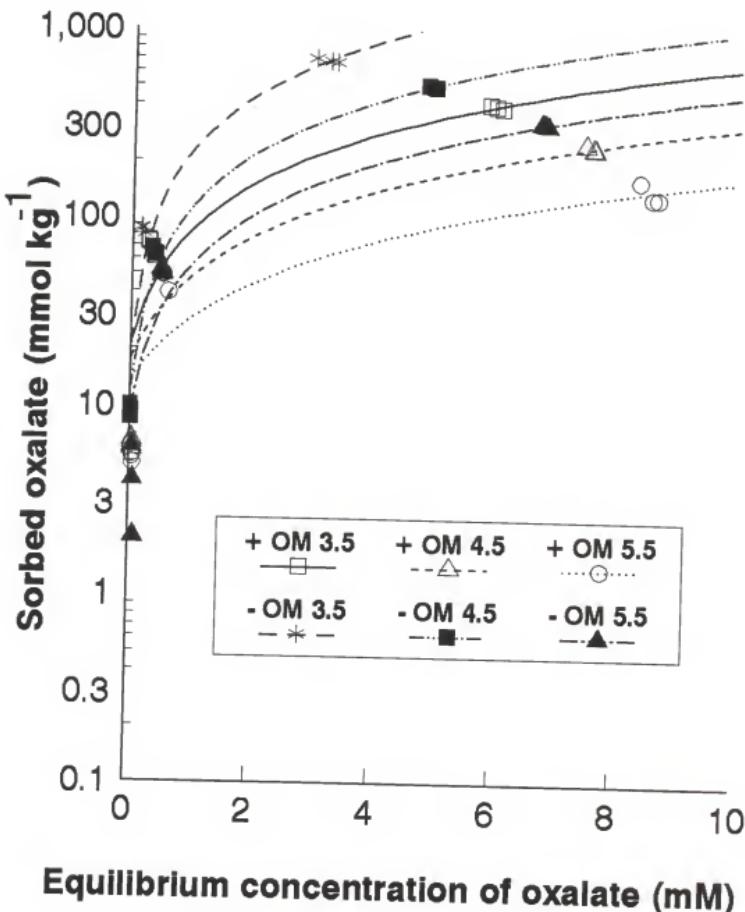


Fig. 2.2 Isotherms for the sorption of oxalate by clay fractions at different pH values.

Table 2.1 Parameters of the linear regression models for oxalate sorption by the clay fractions and the whole-soil samples.

Organic matter	pH	Oxalate sorption		
		Slope	Intercept	R ²
<u>Clay Fractions</u>				
With Organic Matter	3.5	64.3 ^c	21.3 ^a	0.99
	4.5	30.9 ^e	17.8 ^a	0.97
	5.5	15.9 ^f	13.6 ^a	0.96
Without Organic Matter	3.5	209.0 ^a	20.4 ^a	0.99
	4.5	101.4 ^b	11.9 ^a	0.99
	5.5	46.5 ^d	9.2 ^a	0.99
With Organic Matter [@]		36.8 ^b	17.6 ^a	0.79
Without Organic Matter [@]		119.1 ^a	13.9 ^a	0.77
<u>Whole Soil Samples</u>				
With Organic Matter	4.5	0.070 ^b	0.044 ^a	0.94
Without Organic Matter	4.5	0.095 ^a	0.036 ^a	0.95

The same letter in a column at different pH values indicates a lack of significance at the 5 % level within the clay fractions and the whole-soil samples.

@ Includes the combined samples at pH 3.5, 4.5, and 5.5;

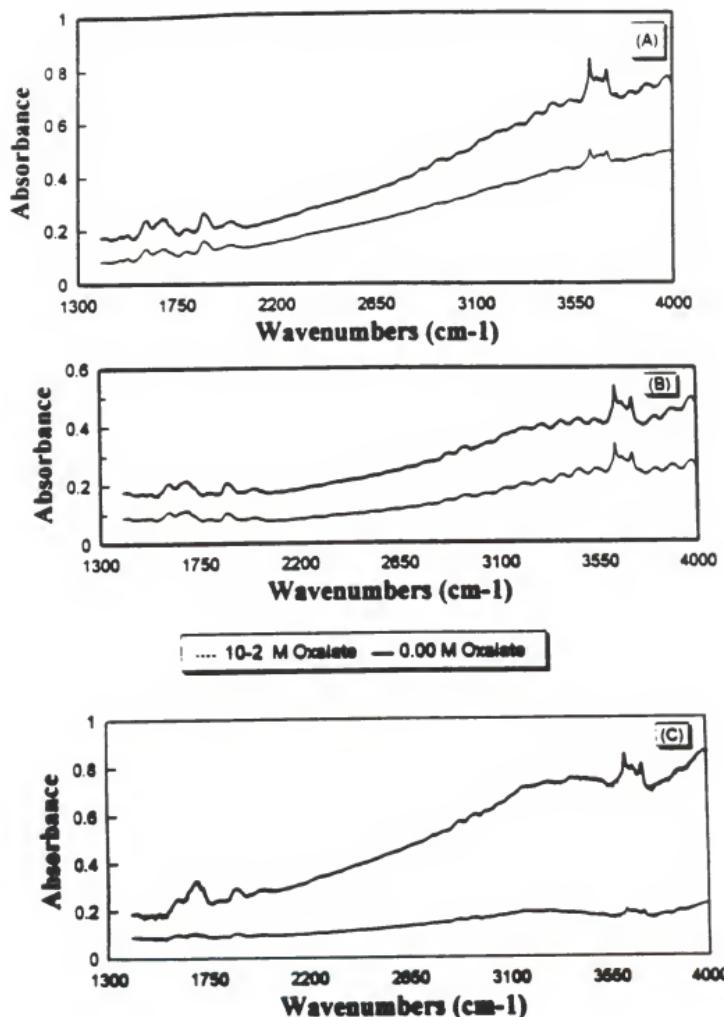


Fig. 2.3 FTIR spectra of clay without organic matter after oxalate sorption at pH 3.5 (A), 4.5 (B), and 5.5 (C).

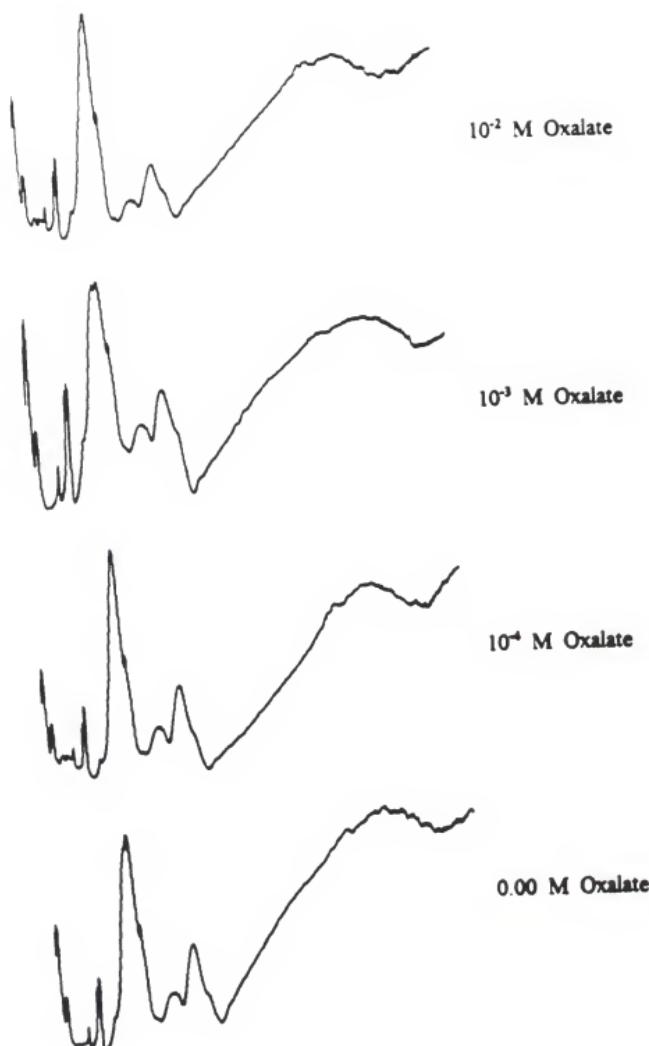


Fig. 2.4 FTIR spectra of clay with organic matter for different concentrations of oxalate sorbed at pH 3.5.

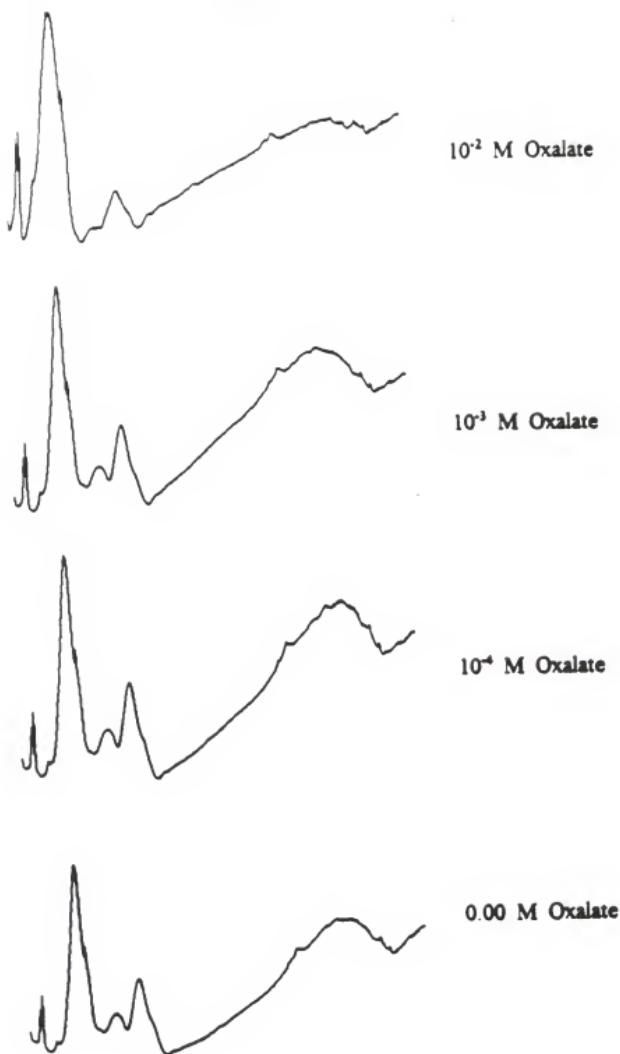


Fig. 2.5 FTIR spectra of clay with organic matter for different concentrations of oxalate sorbed at pH 4.5.

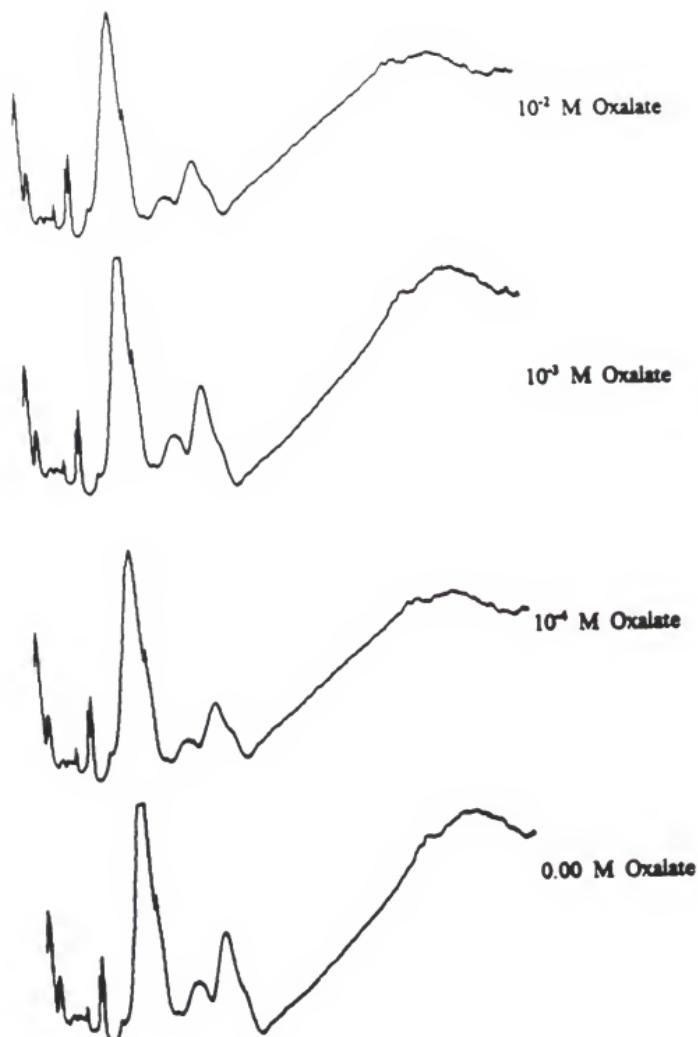


Fig. 2.6 FTIR spectra of clay with organic matter for different concentrations of oxalate sorbed at pH 5.5.

Oxalate Sorption by Whole Soil Samples

Oxalate sorption isotherms for the whole-soil samples are presented in Figure 2.7. The Langmuir model gave the better fit. The parameters of the linearized form of the Langmuir models are presented in Table 2.1. The sorption maxima (S_{\max}) by the whole soil material was 10.57 for soil with organic matter and 14.20 for soil without organic matter. The presence of soil organic matter significantly reduced oxalate sorption.

Release of OH

The sorption of oxalate onto the clay fractions and whole-soil samples released large amounts of OH ions (Fig. 2.8 and Fig. 2.9). Oxalate sorption was significantly and positively correlated with OH ions released (Table 2.2). The OH⁻ release was also significantly influenced by soil organic matter (Table 2.2). The amount of OH ions released at pH 3.5 into solution by the clay fractions was significantly different than the amount of OH ions released into solution at pH 4.5 and 5.5. The FTIR spectra of clay without organic matter showed considerable decrease in the intensity of OH-bands in the region 3000 to 3800 cm⁻¹ following oxalate sorption (Fig. 2.3).

The OH release in solution follows first order kinetics (Figure 2.10) for oxalate sorption by clay surfaces at pH 4.5. Release of OH was initially rapid during the sorption of oxalate (Fig. 2.10), and remained high even after 24 hrs when organic matter was not present. The ratios of moles of OH⁻ released per

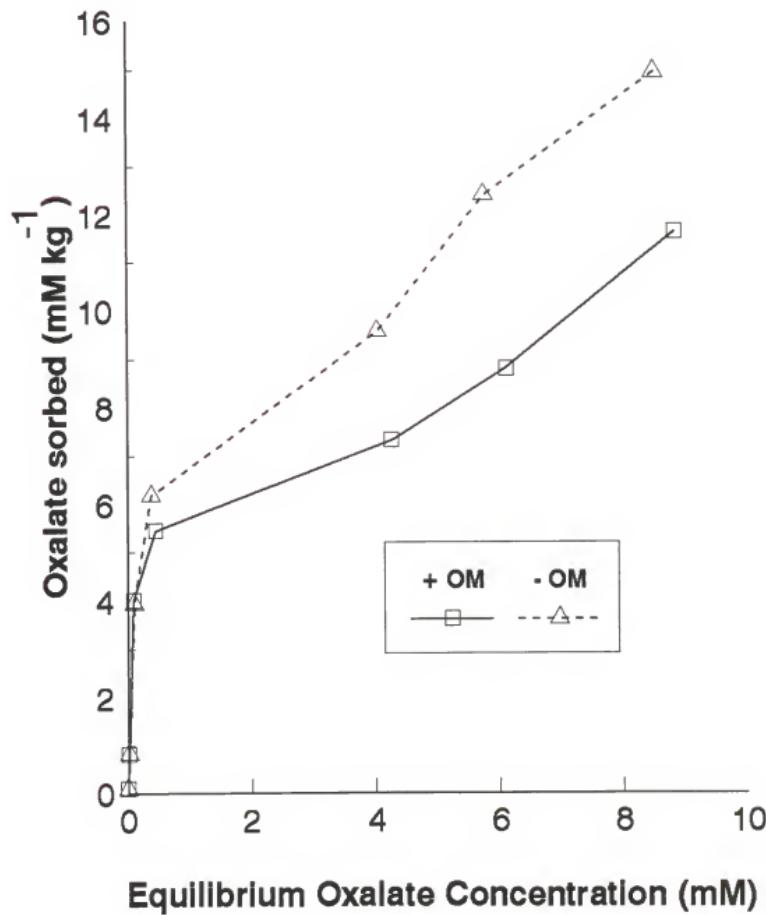


Fig. 2.7 Isotherms for the sorption of oxalate by the whole-soil samples.

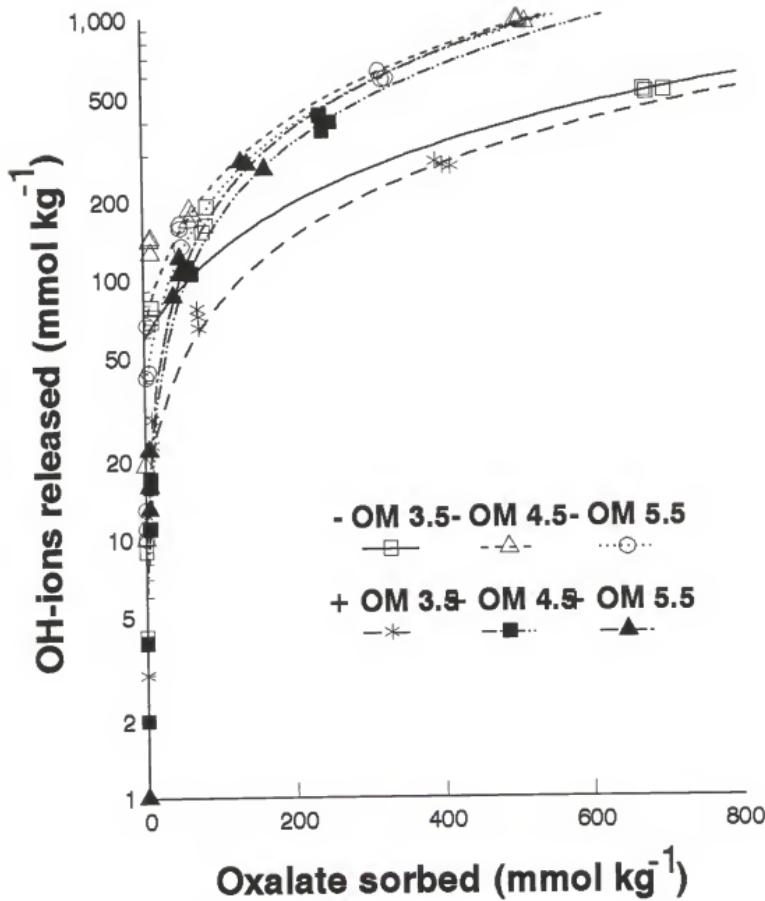


Fig. 2.8

Release of OH ions by the clay fractions at varying pH as a function of oxalate sorption.

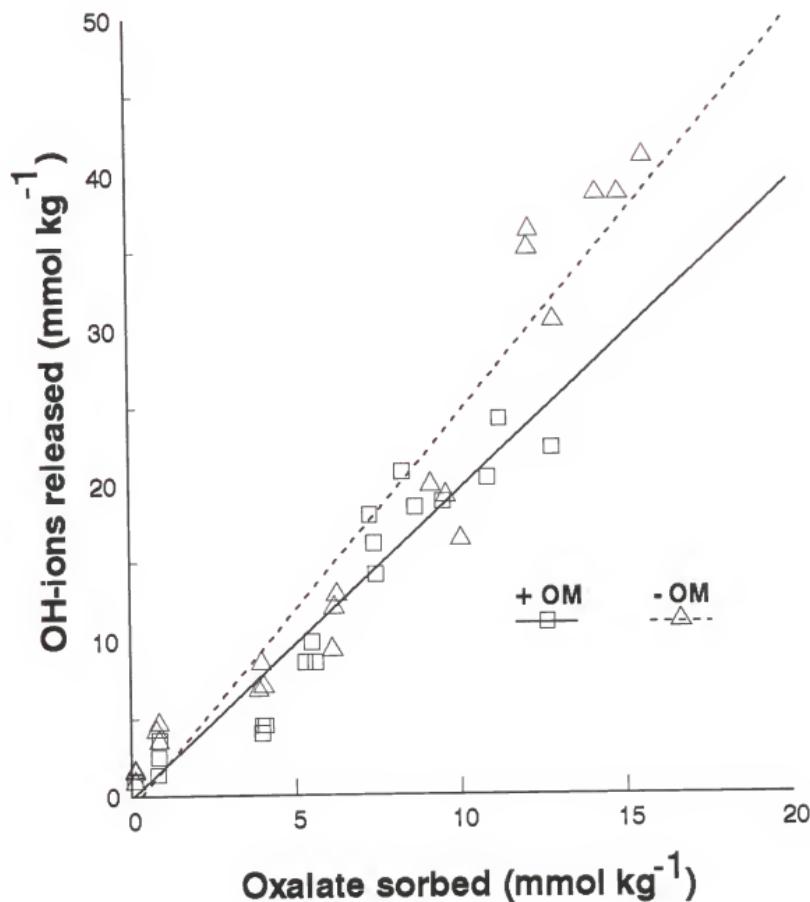


Fig. 2.9 Release of OH ions into solution during the sorption of oxalate by the whole-soil samples.

Table 2.2 Parameters of the linear regression models relating release of OH ions and organic carbon for the clay fractions and whole-soil samples.

Material	OH ions released			Organic carbon released			
	OM/pH	Slope	Intercept	R ²	Slope	Intercept	R ²
<u>Clay fractions</u>							
With organic matter							
3.5	0.65 ^a	13.73 ^a	0.99		0.081 ^a	2.52 ^a	0.99
4.5	1.65 ^b	- 4.07 ^a	0.99		0.131 ^b	6.34 ^b	0.99
5.5	1.88 ^b	1.30 ^a	0.98		0.249 ^c	5.85 ^b	0.99
Without organic matter							
3.5	0.71 ^a	58.4 ^b	0.97				
4.5	1.82 ^b	73.8 ^b	0.99				
5.5	1.73 ^b	40.6 ^b	0.99				
<u>Whole-Soil</u>							
With organic matter							
4.5	1.99 ^b	-0.07 ^b	0.95		0.73	-0.43	0.93
Without organic matter							
4.5	2.48 ^a	-0.14 ^a	0.96				

The same letter in a column at different pH values indicates a lack of significance at the 5 % level within the clay fractions or the whole-soil samples.

@ Includes all samples at pH 3.5, 4.5, and 5.5;

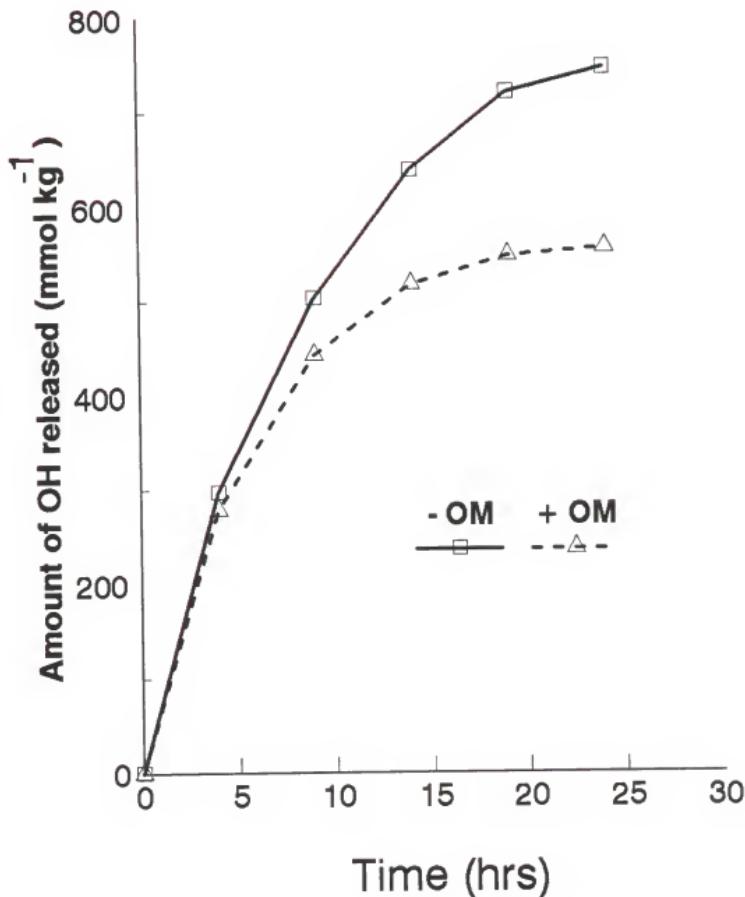


Fig. 2.10 Kinetics of OH^- ions release during the sorption of oxalate by the clay fractions at pH 4.5.

mole of oxalate sorbed are presented in Table 2.3. Average molar ratio at the higher sorption rates was not significantly different from 1.0 at pH 3.5, nor was it significantly different from 2.0 at pH 4.5 and 5.5 for both the clay and whole-soil surfaces.

Release of Aluminum and Iron

The influence of oxalate sorption on the release of Al is presented in Figures 2.11 and 2.12. Aluminum release increased linearly with sorption of oxalate (Table 2.4). The release of Al from whole-soil samples followed a sigmoidal shape, both for samples with and without organic matter (Figures 2.12). Soil organic matter significantly increased Al release, but the release of Al from the clay fractions without organic matter at pH 3.5, 4.5, and 5.5 was not significantly different (Fig. 2.11). Speciation of Al solution in the presence of oxalate was calculated using MINTEQA2. The majority of the Al in solution was present as $[AlL]^+$ and $[AlL_2]^-$ species at pH 4.0 and above (Figure 2.13). The system was undersaturated with respect to both $NaAl(OH)_2(C_2O_4)_3H_2O$ and $Al_3(OH)_7(C_2O_4)_3H_2O$. The concentration of $[AlL_2]^-$ species increased with pH.

The Spodosol used in the study had very low concentrations of total Fe. Iron released from the clay fractions and the whole-soil samples is presented in Table 2.4. The clay fractions and the whole-soil samples with organic matter released a significantly greater amount of Fe than materials without organic matter.

Table 2.3 Ratios of OH⁻ ions released to oxalate sorbed for the clay fractions and whole-soil samples (mean \pm SD; n=3).

	pH	OH released/Oxalate sorbed
<u>Clay fractions</u>		
With Organic Matter	3.5	0.98 \pm 0.03 ^a
	4.5	1.73 \pm 0.11 ^b
	5.5	1.88 \pm 0.22 ^b
Without Organic Matter	3.5	0.86 \pm 0.06 ^a
	4.5	1.96 \pm 0.11 ^b
	5.5	1.85 \pm 0.08 ^b
<u>Whole-Soil Samples</u>		
With Organic Matter	4.5	1.92 \pm 0.21 ^b
Without Organic Matter	4.5	1.86 \pm 0.17 ^b

Superscript "a" and "b" indicate that values are not significantly different from 1.0 or 2 respectively at the 5% level.

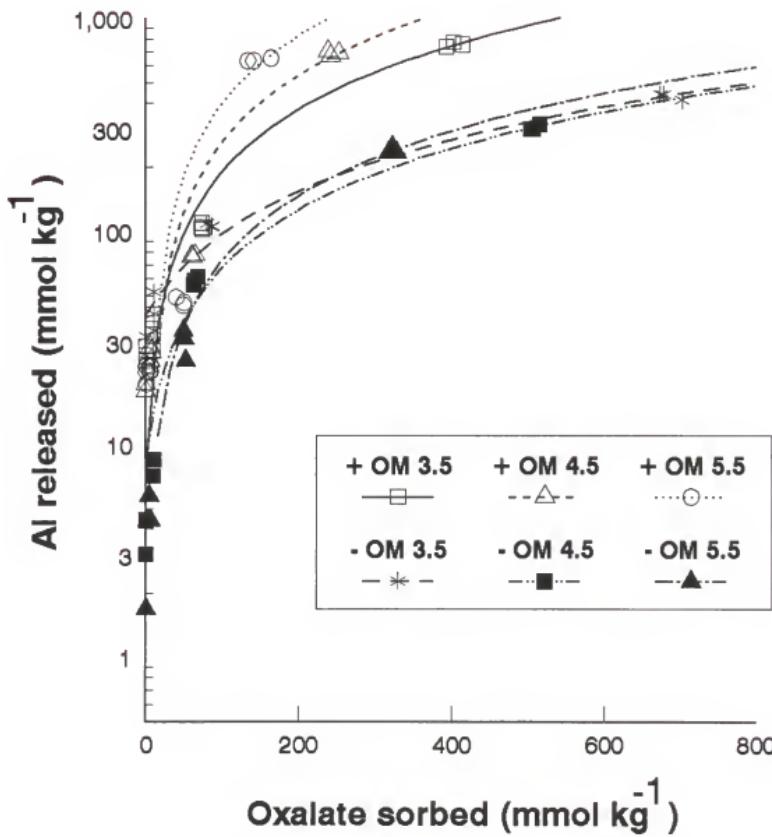


Fig. 2.11 Release of Al from the clay fractions at varying pH as a function of oxalate sorption.

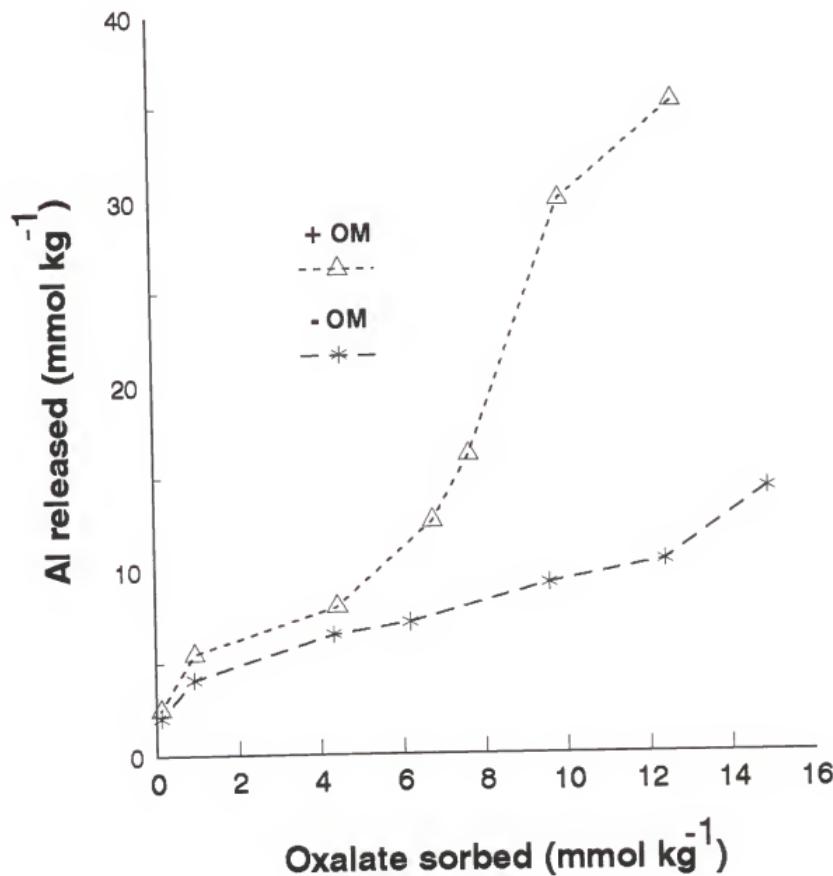


Fig. 2.12 Release of Al from the whole-soil samples as a function of oxalate sorption.

Table 2.4 Parameters of the linear regression models relating release of aluminum and iron with oxalate sorption for the clay fractions and whole-soil samples.

Material	Al release			Fe release		
	OM/pH	Slope	Intercept	R ²	Slope	Intercept
<u>Clay Fractions</u>						
Without organic matter						
3.5	0.57 ^a	40.62 ^a	0.99	0.007 ^a	-0.21 ^a	0.99
4.5	0.59 ^a	8.62 ^a	0.99	0.009 ^b	-0.22 ^a	0.99
5.5	0.74 ^a	-1.03 ^a	0.99	0.012 ^c	-0.15 ^a	0.99
With Organic Matter						
3.5	1.83 ^b	7.11 ^a	0.97	0.008 ^a	-0.19 ^a	0.98
4.5	2.77 ^c	-15.30 ^a	0.99	0.019 ^d	-0.27 ^a	0.97
5.5	4.27 ^d	-28.66 ^a	0.98	0.036 ^e	-0.13 ^a	0.98
With organic matter [@]						
	2.96 ^a	-12.27 ^a	0.93	0.021 ^a	-0.19 ^a	0.73
Without organic matter [@]						
	0.63 ^b	16.07 ^b	0.98	0.010 ^b	-0.19 ^a	0.96
<u>Whole-Soil Samples</u>						
With organic matter						
4.5	0.76 ^b	2.16 ^a	0.96	0.012 ^b	0.025 ^b	0.96
Without organic matter						
4.5	3.07 ^a	-2.75 ^c	0.95	0.042 ^a	-0.061 ^a	0.89

@ Includes all samples at pH 3.5, 4.5, and 5.5;

The same letter in a column at different pH values indicates a lack of significance at the 5 % level within the clay fractions and the whole-soil samples.

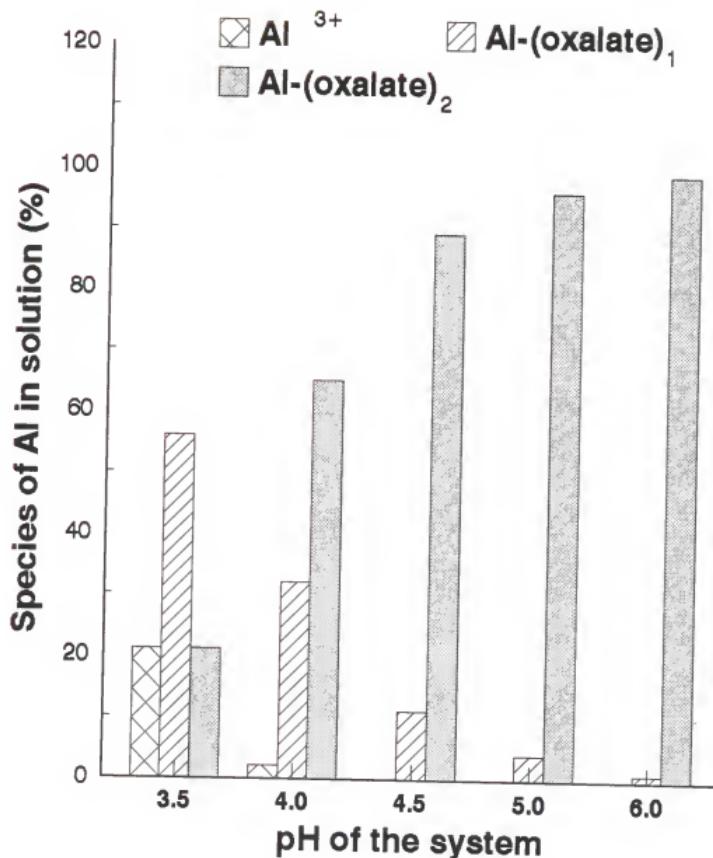


Fig. 2.13 Concentrations of aluminum species in solution at different pH levels in the presence of oxalate.

Release of Organic Carbon

Organic carbon was released from the clay fractions and whole-soil samples in a linear fashion relative to oxalate sorption (Fig. 2.14 and Fig. 2.15). The amount of organic carbon desorption is presented in table 2.2. Seven to ten times more organic carbon was desorbed by 10 mM oxalate as compared to water. The pH of the system also greatly influenced organic carbon desorption, with significantly more organic carbon released at pH 5.5 than at pH 3.5 (0.08 mg g⁻¹ versus 0.249 mg g⁻¹). E4/E6 ratios of the organic carbon released into solution during sorption of oxalate are presented in Table 2.5. The E4/E6 ratio, at the highest loading rate of oxalate (10 mM), decreased to 1.88. There was a linear relationship ($R^2 = 0.99$) between organic carbon release and Al released at pH 3.5, pH 4.5 and 5.5 for the clay fractions (Figs. 2.16 and 2.17).

Spectra for the clay fractions with organic matter showed major absorption bands representing organic carbon in the regions of 3300 cm⁻¹ (O-H and N-H stretching), 2960/2925 cm⁻¹ (aliphatic C-H stretching of CH₃ and -CH₂ groups), 1610 cm⁻¹ (aromatic C=C and/or H-bonded C=O stretching of COOH), and 1400 cm⁻¹ (OH deformation, C-O stretching of phenolic OH, and C-H deformations of CH₃ and CH₂). Intensities of the COOH and CH₃ bands in the spectral region 1610 cm⁻¹ and 1400 cm⁻¹ were calculated at all pH values and at all equilibrium

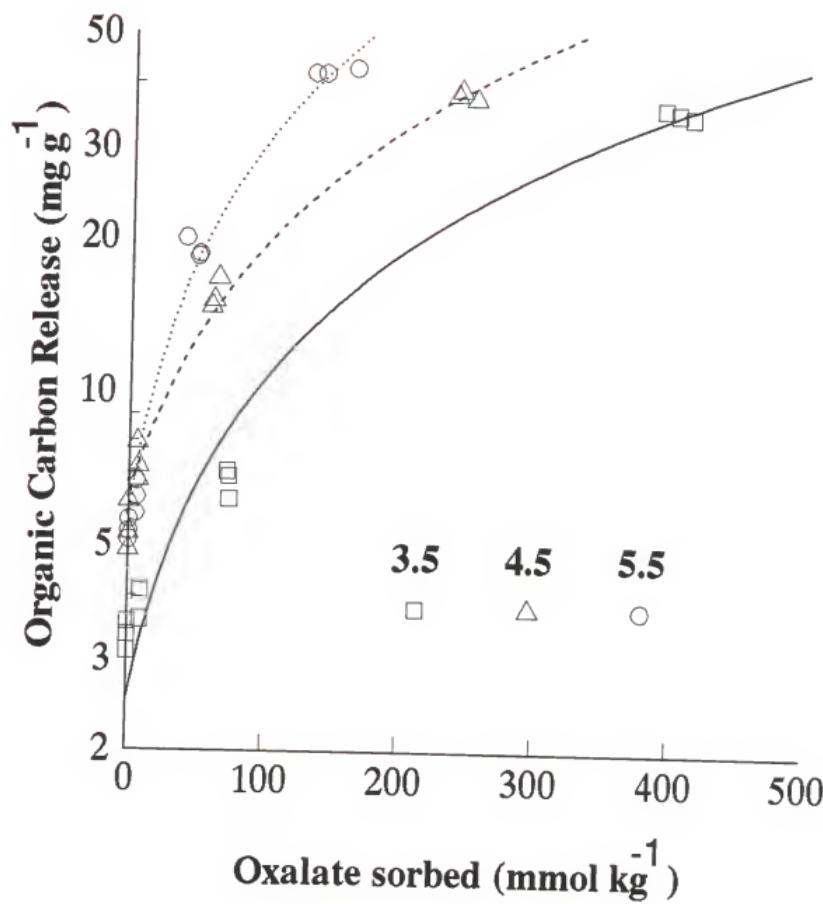


Fig. 2.14 Release of organic carbon by the clay fractions at varying pH as a function of oxalate sorption.

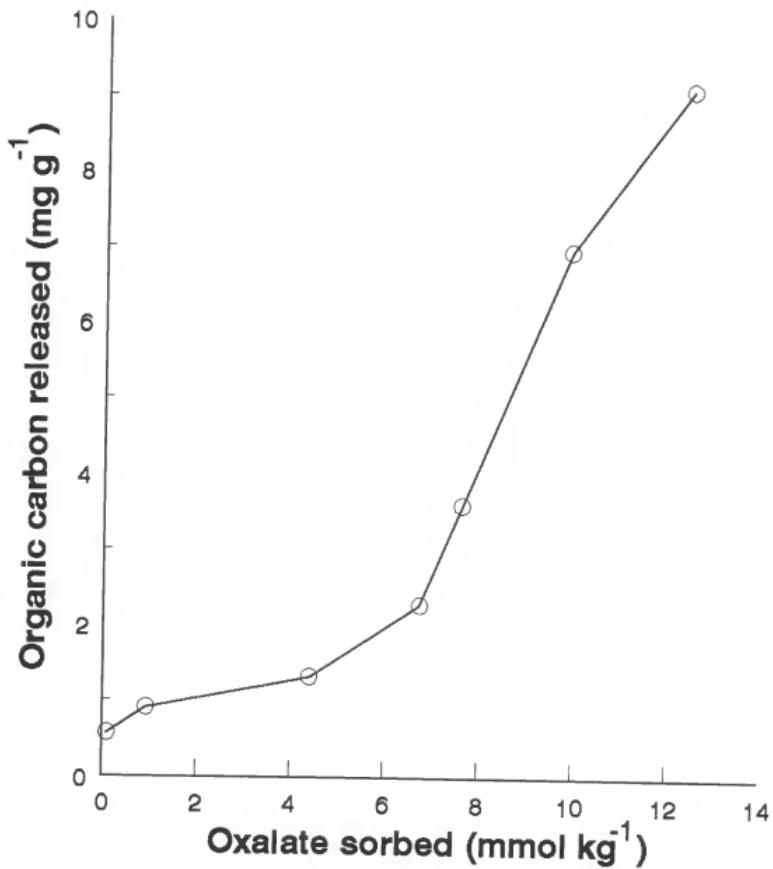


Fig. 2.15 Release of organic carbon from the whole-soil samples as a function of oxalate sorption.

Table 2.5. E_4/E_6 ratio of organic carbon released into solution during the sorption of oxalate by the clay fractions (Mean \pm SD; n=3).

Treatment	Concentration of oxalate added (mM)	E_4/E_6 ratio
3.5	10*	3.15 \pm 0.10
	1.0	7.54 \pm 0.25
	0.1	8.24 \pm 0.56
	0.0	9.26 \pm 0.07
4.5	10	1.88 \pm 0.13
	1.0	7.13 \pm 0.04
	0.1	8.08 \pm 0.13
	0.0	9.07 \pm 0.15
5.5	10	2.14 \pm 0.06
	1.0	6.93 \pm 0.05
	0.1	7.65 \pm 0.21
	0.0	9.07 \pm 0.15

* Concentration of oxalate added into solution

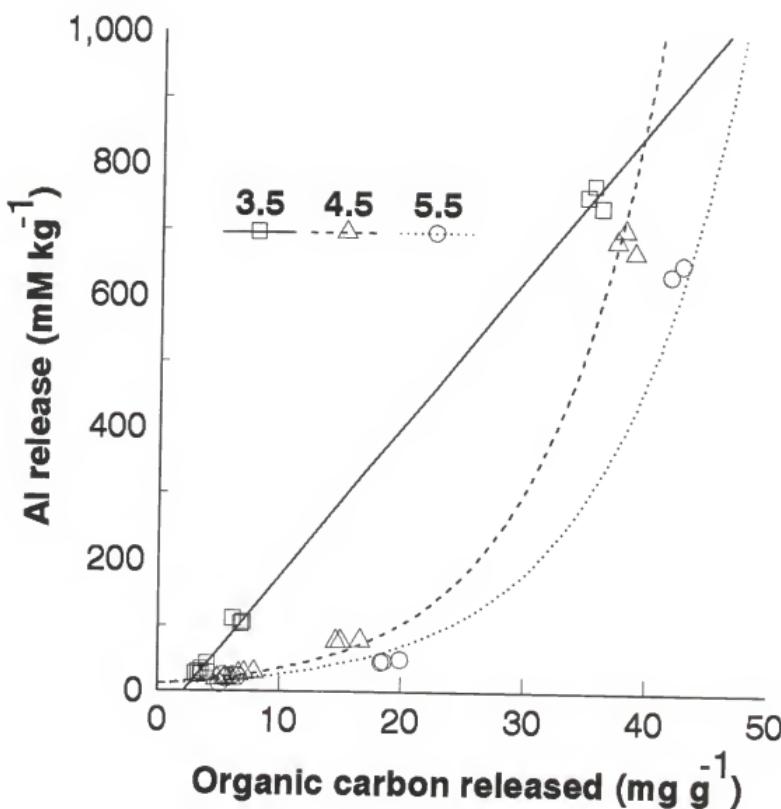


Fig. 2.16 Relationship between Al release and organic carbon release by the clay fraction at varying pH.

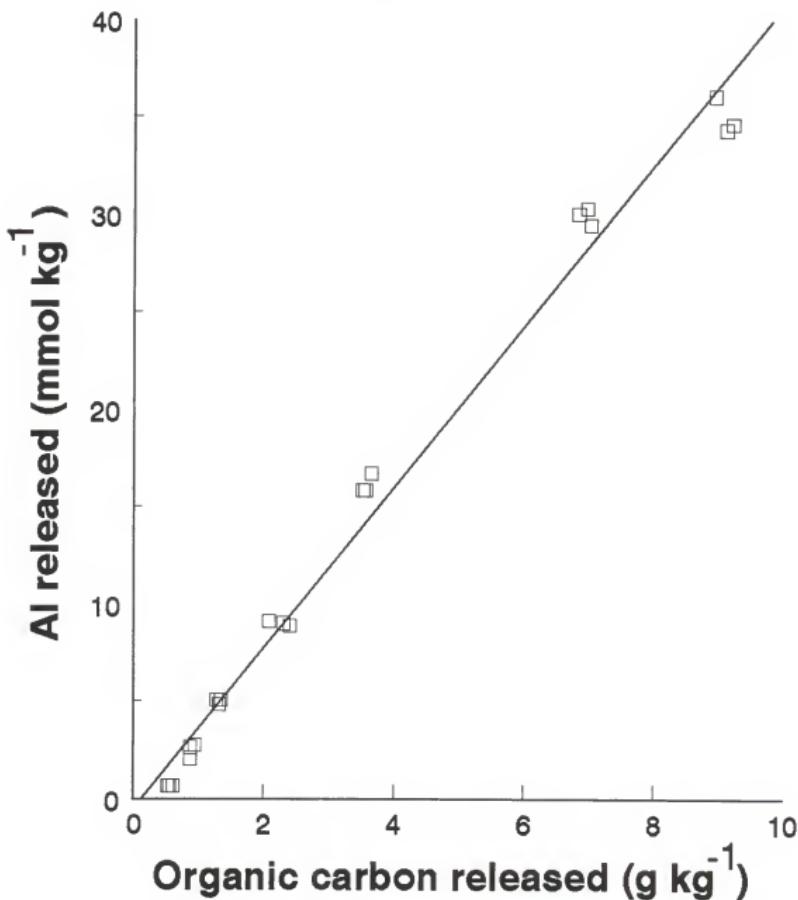


Fig. 2.17 Relationship between Al release and organic carbon release from the whole-soil samples.

concentrations of oxalate. The integrated absorption intensities was normalized with respect to the weight of the clay sample deposited on the AgCl window. Intensity of the 1610 cm⁻¹ (aromatic C=C and/or H-bonded C=O stretching of COOH and CH₃) bands decreased as progressively more oxalate was sorbed by the clay surfaces (Table 2.6, Fig. 2.4, 2.5. and 2.6). The greatest decrease in the intensity of bands at 1610 cm⁻¹ (aromatic C=C and/or H-bonded C=O stretching of COOH) and 1460 cm⁻¹ (OH deformation, C-O stretching of phenolic OH, and C-H deformations of CH₃ and CH₂) corresponded with the maximum oxalate sorption. Decrease in the intensity of these bands was higher at pH 5.5, again corresponding to the pattern of organic carbon release seen in the batch studies. Release of organic carbon was significantly correlated to the intensity of these bands, with R² values of 0.82 to 0.96.

Discussion

Surface Characteristics

Mineralogical analysis using XRD and FTIR data showed that the dominant crystalline clay minerals in the spodic horizon of this Spodosol were kaolinite, HIV and gibbsite. FTIR data established that the clay fraction also contained large amounts of noncrystalline Al oxide. Fox *et al.*, (1990a) reported high amounts of oxalate-extractable (1357 mg/kg) and pyrophosphate-extractable (1379 mg/kg) Al for the same soil. Therefore, both crystalline and amorphous mineral surfaces were available for the sorption of oxalate.

Table 2.6. Intensity of the absorption bands at 1610 cm⁻¹ (aromatic C=C and/or H-bonded C=O stretching of COOH) and 1460 cm⁻¹ (OH deformation, C-O stretching of phenolic-OH, and/or C-H deformations of CH₃ and CH₂) with standard deviations, for clay with organic matter at varying pH values for different amount of oxalate added (Means \pm SD; n=3).

pH	Oxalate added mM	Organic carbon		
		released mg g ⁻¹	V 1610 cm ⁻¹	V 1460 cm ⁻¹
3.5	10.0	35.65 ^a \pm 0.60 ^h	60.74 \pm 4.93	35.05 \pm 3.54
	1.0	6.67 \pm 0.44	74.95 \pm 3.08	40.32 \pm 2.04
	0.1	3.93 \pm 0.29	79.68 \pm 2.37	43.83 \pm 1.65
	0.0	3.34 \pm 0.22	80.40 \pm 4.57	46.85 \pm 4.42
$r = -0.93^a$			$r = -0.93^a$	
4.5	10.0	38.13 \pm 0.56	54.39 \pm 1.04	32.14 1.19
	1.0	15.44 \pm 0.85	72.0 \pm 1.69	42.15 \pm 0.22
	0.1	7.26 \pm 0.45	79.18 \pm 2.95	43.38 \pm 2.19
	0.0	5.42 \pm 0.25	83.76 \pm 8.86	43.65 \pm 3.67
$r = -0.93^a$			$r = -0.95^a$	
5.5	10.0	42.09 \pm 0.74	39.49 \pm 0.19	17.08 \pm 0.45
	1.0	18.95 \pm 1.04	61.78 \pm 2.07	32.78 \pm 3.56
	0.1	6.21 \pm 0.63	67.93 \pm 1.79	37.57 \pm 2.39
	0.0	5.35 \pm 0.61	70.40 \pm 1.74	39.68 \pm 0.60
$r = -0.98^a$			$r = -0.97^a$	

@ Correlation coefficient between organic carbon released and intensity of the absorption bands at 1610 cm⁻¹ at pH 3.5, 4.5 and 5.5.

& Correlation coefficient between organic carbon released and intensity of the absorption bands at 1460 cm⁻¹ at pH 3.5, 4.5 and 5.5.

FTIR data also indicated the presence of a large number of OH functional groups. Since this soil has a very low Fe concentration, we assume that the OH groups were primarily attached to Al. The terminal Al on the mineral surfaces should be Al-OH₂⁺ (aqua), Al-OH (hydroxy), or Al-O⁻ (oxo) groups, depending on pH (Sposito, 1984). Since these spodic horizons have no anion retention capacity, the number of Al-OH₂⁺ (aqua) functional groups is insignificant. In the pH range of this study rules out the significance presence of Al-O⁻, therefore Al-OH (hydroxy) was assumed to be the dominant surface group.

Solution pH determines the oxalate species available for a surface reaction. The dissociation of oxalic acid is:



These pK values would result in dissociation of only one COO⁻ group at pH 3.5, while at pH 4.5 and 5.5 both COO⁻ groups of oxalate would be dissociated. Therefore, at pH 3.5, oxalate should only form monodentate and/or binuclear surface complexes, while at pH 4.5 and 5.5, bidentate surface complexes can be formed.

Oxalate Sorption

Oxalate sorption onto the mineral surfaces may be through ligand exchange and/or precipitation. If the sorption process were dominated by ligand exchange

then we would expect to see several things from these data. First, there should be a release of OH ions accompanying oxalate sorption (Goldberg and Sposito, 1985). This would not be the case if precipitation of oxalate dominated. Second, there should be a linear relationship between the amount of oxalate sorbed and OH ions released into solution. Third, the molar ratio of OH ions released to oxalate sorbed should be approximately 1 or 2. Depending upon pH, a ratio of one would suggest a monodentate or binuclear inner-sphere complex, while a ratio of 2 would suggest a bidentate inner-sphere complex. We would expect a ratio of 1 at pH 3.5, because only one functional group of oxalate is dissociated at this pH and the formation of monodentate and/or binuclear surface complexes is expected. At pH 4.5 and 5.5 we would expect ratios around 2, suggesting that inner-sphere complexes are almost exclusively bidentate.

If precipitation of oxalate were the dominant process we would not expect to see a strong relationship between Al and Fe release into solution and the amount of oxalate sorbed as well as a continuous release of OH⁻ ions into solution with oxalate sorption, even after 24 hrs. The MINTEQA2 speciation calculations indicate that the amount of solid phase species of polynuclear aluminum hydroxy-oxalate complexes ($Al_3(OH)_7(C_2O_4)_3H_2O$ and $NaAl(OH)_7(C_2O_4)_3H_2O$) were insignificant. This implies that precipitation was not the process controlling oxalate sorption in this system. However, this criterion has to be used with caution, as these calculations are based on the assumption that system was at equilibrium which has not been shown to exist in this study.

The data presented here overwhelmingly support the process of ligand exchange. The OH was released in proportion to oxalate sorbed, as shown with both the batch sorption and FTIR measurements. The molar ratio was not statistically different from 1 at pH 3.5 or from 2 at pH 4.5 and 5.5 (Table 2.3). We further conclude that precipitation cannot be a significant factor in oxalate sorption in this study. Al was released into solution in relation to oxalate sorption, showing that oxalate sorption caused Al dissolution rather than precipitation. Also, MINTEQA2 calculations suggested that the oxalate formed soluble Al-oxalate complex in solution and keep it from precipitating. It must be remembered that this was a Na-saturated system without any Ca present on the exchange complex to form insoluble CaC_2O_4 species. Under field conditions, spodic horizon pH is about 3.8 to 4.2, with little Ca present on the exchange complex to interact with native levels of oxalate.

These data further support the conclusion that oxalate is sorbed as monodentate and/or binuclear surface complexes at pH 3.5 ($[\text{mmol OH} / \text{HC}_2\text{O}_4^-] = 1$), but forms predominantly a bidentate complex at higher pH values ($[\text{mmol OH} / \text{C}_2\text{O}_4^{2-}] = 2$). These data support the conclusions of Parfitt *et al.* (1977), who also showed monodentate inner-sphere complex formation of oxalate on goethite surfaces at pH 3.4, at high oxalate concentrations, using infrared spectroscopy. They also suggested formation of a binuclear complex on goethite when oxalate loading rates were low.

Large releases of Al, Fe, and organic carbon during oxalate sorption further suggest a concurrent dissolution reaction. Fox *et al.* (1990a) studied the kinetics of oxalate sorption onto the same soil and reported that oxalate was sorbed during the first 6 hrs while release of Al continued for at least 48 hrs. These data, taken together, support Stumm's (1986) theory of congruent dissolution of mineral surfaces by oxalate following ligand exchange. This constitutes the first such experimental evidence to support Stumm's hypothesis. Oxalate on the clay and whole-soil surfaces forms stable bidentate and binuclear complexes. These complexes involve five- and six-membered rings between the oxalate and Al, which would decrease the strength of the Al-OH-Al bonds and bring Al-oxalate complexes into solution.

The clay fractions and whole-soil samples with organic matter released more Al, respectively than did the clay or soil without organic matter. Another source of Al released from the clay and soil with organic matter was the Al present as metal-organic complexes. Lee *et al.*, (1988b) studied the forms of aluminum in selected Florida Spodosols and found that more than 75 % of the Al in spodic horizons was present as Al-fulvate. Aluminum can act as a bridge between soil particles and organic matter. If oxalate solubilizes Al through the formation of stable, soluble, Al-oxalate complexes in solution, then this could result in increased Al release.

Effect of Organic Carbon on Oxalate Sorption.

The removal of organic carbon increased the sorption of oxalate. This can be attributed to either competition between organic carbon and oxalate for same sorption sites or formation of new sorption sites on mineral surfaces when H_2O_2 was used to oxidize the organic carbon. These data do not differentiate between these possibilities; however, either option would enhance the surface area for oxalate sorption. Zelazny and Quresih (1973) reported that H_2O_2 treatment of clay material from Florida soils enhanced surface area and decreased surface charge. This evidence suggests that, with the removal of organic matter, surface area would increase somewhat resulting in greater sorption of oxalate by clay and soil surfaces without organic matter.

CHAPTER 3

INFLUENCE OF OXALATE AND SOIL ORGANIC MATTER ON SORPTION OF PHOSPHORUS ONTO A SPODIC HORIZON

Introduction

Phosphorus deficiencies are common on the poorly-drained Spodosols of the flatwoods region of the lower Coastal Plain of the Southeastern United States (Pritchett and Comerford, 1983; Comerford *et al.*, 1984). P availability depends on physico-chemical properties such as P sorption by colloidal surfaces. Organic ligands are continuously released into the rhizosphere by decaying plants and animals, through microbial processes, and as root exudates (Stevenson, 1982; Fox and Comerford, 1990). The supply of P to plants is strongly influenced by the presence of these organic ligands. Different organic anions have been reported to modify the sorption of phosphate by soils and soil components (Deb and Datta, 1967; Earl *et al.*, 1979; Kafkafi *et al.*, 1988).

Aluminum and iron, either in solution or as crystalline/amorphous soil constituents, are the principal agents responsible for chemical fixation of phosphate in acid soils (Yuan and Lavkulich, 1994). Organic anions which are capable of forming stable complexes with aluminum and iron in solution (Appelt *et al.*, 1975; Viotante and Huang, 1985; Traina *et al.*, 1986a, 1986b; Huang and Schnitzer,

1986; Comerford and Skinner, 1989) or on mineral surfaces (Pohlman and McColl, 1986; Stumm, 1986; Kafkafi *et al.*, 1988; Martell *et al.*, 1988; Fox *et al.*, 1990b) can be effective in reducing the P sorption capacity of soils. Phosphate sorption was reduced in the presence of humic acids, fulvic acids, and low molecular organic acids while each of these compounds were specifically sorbed onto pure mineral surfaces (Nagarajah *et al.*, 1968, 1970; Sibanda and Young, 1986; Ryden and Syers 1987; Moore *et al.*, 1992; and Violante and Gianfreda, 1993). However, little work has documented the effect of oxalate and soil organic matter on the sorption of P using soil materials.

The ability of different organic anions to compete with P for sorption sites on the surfaces of soil components was reported to be greatest at a pH equivalent to the pK_{a2} of the organic acid (Hingston *et al.*, 1967; Hingston *et al.*, 1972). Soil organic acids which contain carboxylic (-COOH) and/or phenolic (-OH) functional groups can bind to oxide surfaces, thereby reducing the number of surface sites available for P sorption (Yuan, 1980). This also alters electrostatic charge at the solid surface. Both of these interactions of organic anions are influenced by the solution pH, relative concentrations of different anions which may be present and intrinsic affinities of these anions for the mineral surfaces. The pH of the system is important in surface and solution complexation reactions as it will i) regulate the concentrations of various P and organic anion species which differ in their affinity for the solid surface, ii) affect the charge density of solid

surfaces, and iii) control the competition between OH⁻, P and organic anions for common adsorption sites (Barrow, 1987; Kafkafi *et al.*, 1988).

Poorly-drained Spodosols are the dominant soil type in the flatwoods of Florida's lower Coastal Plain. Among the low-molecular weight organic anions present in these soils, the most abundant is oxalate (Fox and Comerford, 1990). Earlier work by various researchers indicated that the specific sorption of phosphate and organic ligands like oxalate is through ligand exchange (Goldberg and Sposito, 1985). This process should result in the release of OH⁻. The amount of OH⁻ released during a sorption reaction in turn depends upon the characteristics of the surfaces, concentrations of the adsorbing species, and solution pH. The change in solution concentration of OH⁻ ions can be used to identify the types of complexes formed on the various solid surfaces.

Organomineral complexes have an important influence on the physical and chemical properties, and reactivity of soil particles (Viotante and Huang, 1984; Viotante and Huang, 1985; Huang and Schnitzer, 1986). The main clay minerals present in flatwoods soils are quartz, kaolinite, gibbsite and hydroxy-interlayered vermiculite (HIV) (Harris *et al.*, 1987a). Since Florida soils are sandy, these minerals are present as coatings on the sand particles (Harris *et al.*, 1987a; 1987b). The binding materials for these clay-sized mineral particles to sand grains is reported to be an Al dominated gel-like substance (Lee *et al.*, 1988a). Lee *et al.* (1988b) further indicated that Al acts as a cementing material, probably as Al-fulvate. The Spodosols of the lower Coastal Plain are known to have high

concentrations of amorphous Al oxides and are classified as Alaquods. Organic substances which are present as surface coatings and/or acting as cementing material can significantly affect the retention of P by modifying the specific surface area and surface charge of crystalline and noncrystalline minerals in the finer fractions of the Spodosols. Therefore, it is important to investigate the sorption of P by this highly reactive component.

Recently, studies were carried out to investigate the sorption of P by organo-mineral complexes. Violante and Huang (1989) studied the sorption of P on precipitated-Al products formed in the presence of organic ligands (citrate, tartrate, malate, aspartate and tannate). They found that the amount, the nature and the size of organic ligands coprecipitated with Al, as well as the surface properties of Al-organic ligand complexes, strongly influenced P sorption capacity. Haynes and Swift (1989) investigated the effect of pH on P sorption onto Al-organic matter complexes. They reported that increase in pH greatly increased P sorption capacity. These studies were performed on pure minerals. However in soils, many minerals coexist, and were formed in the presence of different organic compounds. Therefore, P sorption properties of these minerals could be considerably different from those of the pure minerals.

The purpose of the present investigation was to study: i) P sorption by the clay fraction and the whole-soil samples of a spodic horizon, and ii) the influence of oxalate and soil organic matter on P sorption in a such system.

Materials and Methods

Soil Material

Soil was collected from the spodic horizon (Bh) of a single soil pit of a Pomona series (sandy, siliceous, hyperthermic, Ultic Alaquod) at the Gator Nationals Forest site located in Alachua County, Florida. The soil material was air-dried, passed through a 2-mm sieve and stored in plastic bags. Particle-size analysis of the sample was carried out using standard methods (Page *et al.*, 1986). The soil contained 91 % sand, 8 % silt and 1 % clay.

Preparation of Whole-Soil Sample and the Clay Fractions

The preparation of whole-soil samples for the sorption experiment was previously described in Chapter 2. The water-dispersible clay fraction was separated (Genrich and Bremner, 1974) as reported in Chapter 2. Both the whole-soil and clay samples were dried at 110 °C.

Sorption Studies on Clay Fraction and Whole Soil

Sorption of Phosphate Alone

Sorption experiments were carried out over a range of phosphate concentrations at pH 4.5 using a batch procedure. Triplicate 250 mg samples of clay (with and without organic matter) were placed in 30 ml bottles with 25 ml of solution having a phosphate concentration of 0 mM, 0.1 mM, 1.0 mM, or 10 mM adjusted initially to pH 4.5 (using 0.1 M HCl or NaOH). Triplicate five-gram

sample of whole soil from each treatment (with or without organic matter) were placed in 100 ml bottles with 50 ml of solution having a phosphate concentration of 0 mM, 0.1 mM, 0.5 mM, 1.0 mM, 3.0 mM, 7.0 mM or 10 mM adjusted initially to pH 4.5 (using 0.1 M HCl or NaOH).

Sorption of Phosphate and Oxalate Added as a Mixture

Sorption experiments were carried out at different oxalate to phosphate molar ratios. The concentration of oxalate used was 1.0 mM with a phosphate concentration of 0 mM, 0.1 mM, 1.0 mM, or 10 mM for the clay samples. For the whole-soil sample with and without organic carbon, an oxalate concentration of 1.0 mM was used, with a phosphate concentration of 0 mM, 0.1 mM, 0.5 mM, 1.0 mM, 3.0 mM, 7.0 mM or 10 mM. pH of the clay suspensions and the whole-soil suspensions was initially adjusted to 4.5 using 0.1 M HCl or NaOH.

Two drops of toluene were added to inhibit microbial growth, and the samples were placed in a reciprocating shaker for 24 hrs. pH values of the suspensions were periodically (every three hours) adjusted to 4.5 with 0.1 M HCl or NaOH over the 24 hrs of the experiment. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. The resultant supernatant solutions were used for analysis of oxalate, Al, Fe, inorganic P, and organic carbon. Sorbed P and oxalate were calculated from the difference between the initial and final concentrations in solution. The adsorbate was saved for further experiments, as described in Chapter 4.

Chemical Analysis

Solution pH was measured using a combination glass electrode in conjunction with an Orion pH meter. Aluminum was determined using a flame emission spectrophotometer with $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame whereas Fe was detected with a C_2H_2 flame. Total organic carbon content of the clay sample with organic matter was measured via persulfate oxidation and IR analysis of the resultant CO_2 using on a TOC apparatus (College Station, TX). E4 ($\lambda=465$) to E6 ($\lambda=665$) ratios of the organic carbon released into solution from the clay with organic matter were measured using a Shimadzu UV/Vis spectrophotometer.

Oxalate in the extract was determined by HPLC (Fox and Comerford, 1990), using a Hamilton PRP-X300 150 x 4.1 mm organic acid column (Hamilton Co., Reno, Nevada) along with a Gilson single piston high pressure pump and a Pheodyne model 7125 injection valve fitted with a 20 μL injection loop. The HPLC system used a Gilson Holochrom variable wavelength UV detector in conjunction with a Gilson computerized integrator. Eluent was 0.005 M H_2SO_4 at a flow rate of 2 mL min^{-1} . Oxalate concentration was calculated from the calibration curve obtained with standard solutions of 0.1 to 10 mmol L^{-1} .

Inorganic P in the filtrate was determined by a molybdenum-blue colorimetric procedure using ascorbic acid as the reductant (Murphy and Riley, 1962). This is an operational definition of inorganic P, for molybdenum may also hydrolyze some organic P (Stainton, 1980).

Titration Curves for the Clay and Soil Samples

To determine the amount of OH^- ions released into solution during the sorption of P and/or oxalate, titration curves were prepared for each clay and whole-soil sample (with and without organic matter). Duplicate one-gram samples of clay and 10-gram samples of soil were equilibrated with 100 mL of water adjusted to pH 3.0. The suspension was allowed to equilibrate for 24 hrs, titration then being carried out (with 0.1 N NaOH) from pH 3.0 to 7.0. With each addition of 0.1 ml NaOH, the solution was allowed to equilibrate for 2 to 5 minutes or until the pH stabilized. pH buffer curves, relating the change in pH with unit addition of NaOH over the pH range 4.40 to 6.00, were calculated. Curves were fit to the data and used to calculate the amount of OH^- ions required to change pH of the soil and clay systems to specific values.

Adsorption Isotherms

The Langmuir adsorption model was fit to the sorption data. The following equation was used:

$$S = \frac{S_m K C}{1 + K C} \quad (3.1)$$

where S is the amount of P or oxalate taken up per unit mass of clay or soil (mM kg^{-1}), S_m is the maximum amount of P or oxalate that was bound, C is the equilibrium concentration of P/oxalate (mM), and K is a constant related to the

binding energy of P or oxalate sorption. The parameters (K and S_m) were calculated by a least square fit of the linear form of the equation:

$$\frac{C}{S} = \left[\frac{1}{KS_m} \right] + \frac{C}{S_m} \quad 3.2$$

Speciation Calculations

The metal speciation model MINTEQA2 version 3.2 was used to calculate the species of Al and P in the solution. It was assumed that the system had achieved equilibrium conditions. Although the total activity of Al ions was not known, the assumed activity of Al from the congruent dissolution by oxalate was used (Chapter 2) to estimate the saturation level with respect to an amorphous aluminum phosphate solid phase. Calculations were carried out at solution P concentrations corresponding to the highest loading rate of P (10^{-2} M). The formation constants used for calculations of species were those of the MINTEQA2 data base taken from Martell and Smith (1982).

Statistical Analysis

The linear form of the Langmuir equation was used to test the differences between parameters for P sorption. Statistical differences among regression lines for the desorption of Al, Fe, OH, and organic carbon during P sorption were tested using the General Linear Models procedure of the SAS framework (SAS Institute, 1985). The model used was:

$$Y_{ij} = \alpha + \beta X_{ij} + \epsilon_{ij} \quad (3.3)$$

where α is the intercept, β is the slope of the line and ϵ is the error term. To compare two regression lines, the α and β values of the two lines were compared. ANOVA and t-test were used to test the difference between α_1 and α_2 well as between β_1 and β_2 . The significance of the difference between two means was determined using a t-test (Snedecor and Cochran, 1980). Standard deviations or standard errors of means are given, when appropriate.

Results

Sorption of P

Clay Fractions

Sorption isotherms for phosphate sorption onto clay samples with and without organic matter are presented in Fig. 3.1. The presence of oxalate and soil organic matter significantly reduced P sorption. Maximum reduction in P sorption (about 50 %) was observed when both organic carbon and oxalate were present in the system. The P sorption data, for the range of concentrations studied, conformed to the Langmuir equation. Sorption parameters for the Langmuir equation are presented in Table 3.1.

Whole-Soil Samples

Phosphate sorption isotherms are presented in Figure 3.2. Sorption

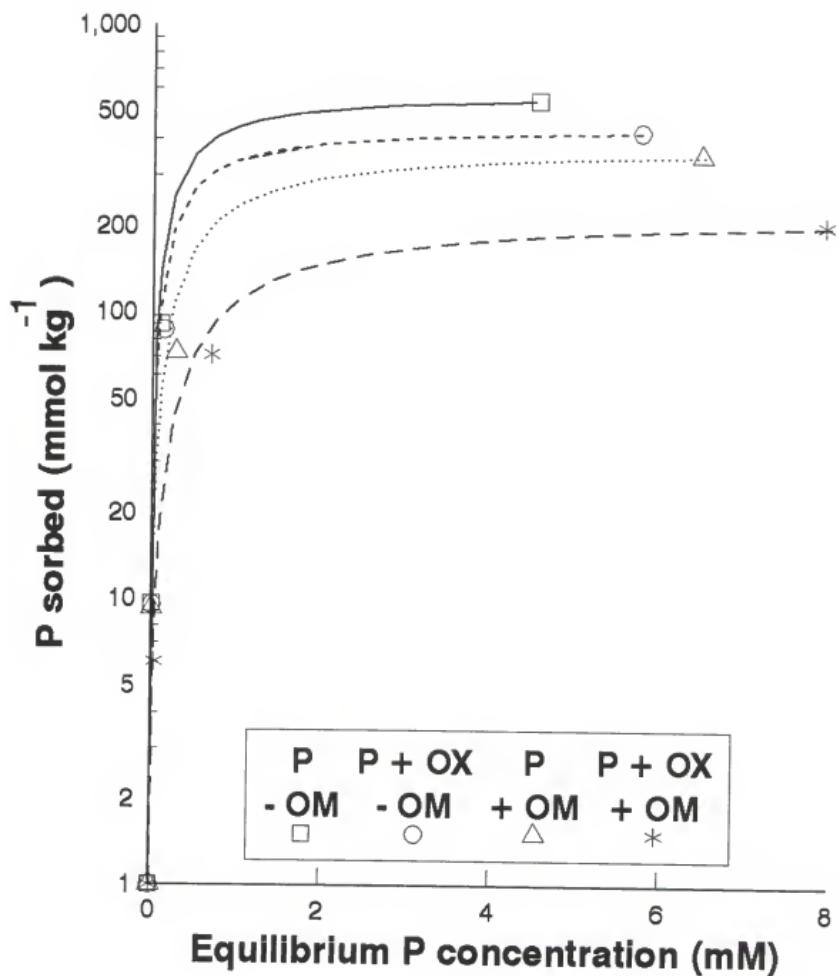


Fig. 3.1. Isotherms for the sorption of P by the clay fractions.

Table 3.1. Langmuir sorption isotherm parameters for P sorption onto the whole-soil samples and clay fractions with and without organic matter.

		Langmuir Model			
Treatments	Anion	Sorption Maxima S_{Max} (1/b)	Intercept 1/SmK	Sorption energy K	R^2
Soil without organic matter					
P	P	29.33 ^c	0.051 ^a	0.66	0.88
P+OX	P	20.08 ^b	0.042 ^a	1.18	0.97
Soil With Organic Matter					
P	P	17.39 ^b	0.035 ^a	1.62	0.98
P+OX	P	13.83 ^a	0.052 ^a	1.39	0.98
Clay without organic matter					
P	P	588.0 ^d	0.0005 ^a	3.32	0.97
P+OX	P	454.0 ^c	0.0022 ^a	2.42	0.99
Clay with organic matter					
P	P	379.0 ^b	0.0013 ^a	1.90	0.98
P+OX	P	328.0 ^a	0.0047 ^a	0.64	0.99

* Values within columns followed by same letter for the whole-soil or clay samples are not significantly different at the 5% level

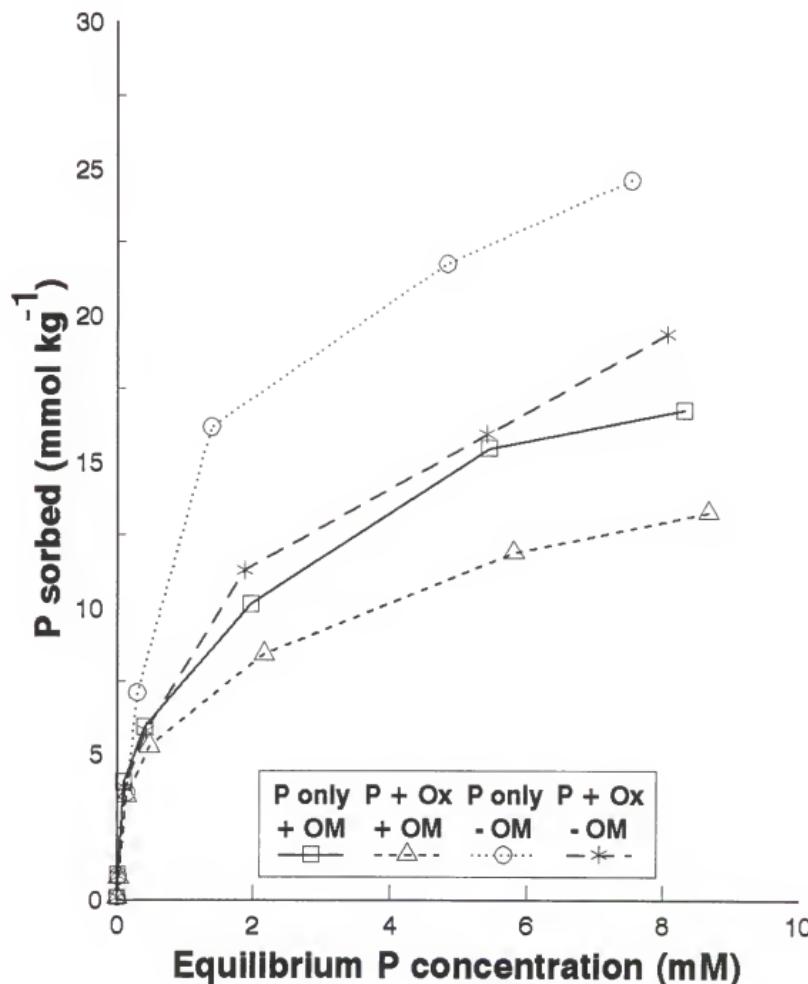


Fig. 3.2 Isotherms for the sorption of P by the whole-soil samples.

parameters for the Langmuir model are presented in Table 3.1. In the case of the whole-soil samples, P sorption maxima were significantly reduced by soil organic matter. The presence of soil organic matter and oxalate significantly reduced P sorption by both types of soil material.

P sorption parameters of the clay samples also were recalculated on a whole-soil basis (assuming a clay % for the whole soil = 1.3 %), and compared to the P sorption parameters of whole-soil samples. Significantly more P was sorbed by the whole-soil samples than by the clay samples when reported on a whole-soil basis (Table 3.2). P sorption by whole-soil samples was 3 to 10 times higher than that of the clay samples.

Sorption of Phosphate in the Presence of Oxalate

Less P was sorbed by the clay fractions and whole-soil samples in the presence of oxalate (Table 3.3). The percent efficiency of oxalate in reducing P sorption was calculated according to the expression of Deb and Datta (1967):

$$Ox_e = [1 - \frac{P_{ox}}{P_o}] \times 100 \quad (3.4)$$

where Ox_e is the efficiency of oxalate in reducing P sorption (%), P_{ox} is the P sorbed in the presence of oxalate, and P_o is the P sorbed alone. The efficiency of oxalate in reducing P sorption increased as the concentration of P in solution increased (Table 3.4).

Table 3.2. P sorption onto the whole soil material compared to P sorbed onto the clay fraction expressed on a whole soil basis (Mean \pm SD; n=3).

Treatment	Conc of anions added (mM)	P sorption (mmol kg ⁻¹)			
		Whole soil	+ OM Clay Fraction	Whole soil	- OM Clay fraction
P alone	10	16.7 \pm 0.27 ^a	4.58 \pm 0.05 ^b	24.6 \pm 0.5 ^a	7.09 \pm 0.07 ^b
	1.0	5.9 \pm 0.13 ^a	0.94 \pm 0.01 ^b	7.1 \pm 0.06 ^a	1.17 \pm 0.01 ^b
	0.1	0.9 \pm 0.02 ^a	0.12 \pm 0.01 ^b	0.8 \pm 0.01 ^a	0.12 \pm 0.01 ^b
P + Ox	10+1	13.3 \pm 0.25 ^a	3.52 \pm 0.04 ^b	19.3 \pm 0.37 ^a	5.95 \pm 0.04 ^b
	1.0+1	5.3 \pm 0.14 ^a	0.79 \pm 0.01 ^b	5.8 \pm 0.05 ^a	0.96 \pm 0.01 ^b
	0.1+1	0.78 \pm 0.02 ^a	0.09 \pm 0.01 ^b	0.8 \pm 0.01 ^a	0.08 \pm 0.001 ^b

+ OM = with organic matter and - OM is without organic matter

@ Values within each row for each material with organic matter and without organic matter are significantly different (P = 0.05) if followed by a different letter

Table 3.3. Amount of Al, Fe and organic carbon released into solution with P + oxalate sorption onto the whole-soil samples and the clay fractions (Mean \pm SD; n=3).

P + Ox Ratio	With Organic Matter					Without Organic matter			
	Oxalate --- (mmol kg ⁻¹)---	Sorbed			Released (mg g ⁻¹)	Oxalate ----- (mmol kg ⁻¹)-----	Sorbed		
		Al	Fe	O. Carbon			Al	Fe	
<u>Whole-Soil samples</u>									
10:1	4.2 \pm 0.11	8.72	0.044	1.44		5.0 \pm 0.10	5.01	0.079	
7:1	4.8 \pm 0.15	6.99	0.034	1.30		5.4 \pm 0.08	5.40	0.082	
3:1	5.2 \pm 0.06	7.33	0.027	1.21		5.9 \pm 0.15	5.44	0.087	
1:1	5.4 \pm 0.10	7.60	0.029	1.12		6.0 \pm 0.04	6.26	0.101	
0.5:1	5.5 \pm 0.11	7.83	0.037	0.97		6.1 \pm 0.05	6.49	0.101	
0.1:1	5.5 \pm 0.08	7.87	0.034	0.62		6.1 \pm 0.02	6.64	0.104	
<u>Clay fractions</u>									
10:1	32.9 \pm 1.88	24.45	0.44	166		22.4 \pm 2.05	14.19	0.23	
1:1	38.8 \pm 0.83	18.91	0.31	125		36.7 \pm 3.50	14.46	0.31	
0.1:1	42.2 \pm 0.52	19.45	0.12	117		50.42 \pm 1.65	14.59	0.30	

Table 3.4. Effect of oxalate in reducing the sorption of P onto whole-soil samples and the clay fractions (Mean \pm SD; n=3).

P:Oxalate ratio	% reduction in P sorption	
	With OM	Without OM
<u>Whole soil</u>		
10:1	20.7 \pm 3.5 ^{aa}	21.3 \pm 3.5 ^{ba}
7:1	22.5 \pm 4.7 ^{aa}	26.6 \pm 2.9 ^{ba}
3:1	16.7 \pm 5.7 ^{ab}	30.2 \pm 3.7 ^{aa}
1:1	10.8 \pm 4.4 ^{aa}	18.4 \pm 0.4 ^{ba}
0.5:1	1.2 \pm 1.0 ^{ba}	-5.3 \pm 0.5 ^{cb}
0.1:1	1.2 \pm 0.8 ^{ba}	-0.9 \pm 0.3 ^{da}
<u>Clay fraction</u>		
10:1	23 \pm 2 ^{aa}	22 \pm 0.5 ^{aa}
1:1	16 \pm 1 ^{ba}	5 \pm 0.5 ^{bb}
0.1:1	2 \pm 2 ^{ca}	1 \pm 1 ^{ca}

The first superscript letter indicates significant differences within a column and material, while the second letter indicates significant differences between rows.

Release of OH⁻

OH⁻ ions were released into the system with the sorption of P alone or P + oxalate (Fig 3.3 and Fig. 3.4). For the clay samples, P and oxalate together released more OH⁻ into solution than P alone (Table 3.5). The kinetics of OH⁻ ions release are presented in Figure 3.5 for the P alone, and P + oxalate, treatments with the clay. Approximately 80% of the OH⁻ release accompanying P sorption was detected in the first 8 hrs. For clay with organic matter, the release of OH⁻ accompanying P sorption was initially rapid and reached equilibrium after 14 hrs.

The molar ratio of OH⁻ released per mole of P sorbed was between 0.85 and 1.38 for the clay fractions (Table 3.6). A similar range was observed for the whole-soil samples. On average, the ratio was not significantly different from 1 for P sorption alone but was significantly higher than 1 for sorption of P + oxalate.

Release of Organic Carbon

There was a linear relationship between the amount of organic carbon released and the sorption of anions by the whole-soil samples and the clay fractions (Table 3.5). During sorption of P by the clay or soil, a small amount of organic carbon was released into solution. The presence of oxalate with the P did not significantly affect organic carbon release (Table 3.5). The E4/E6 ratio of released organic matter was approximatly 9.0 during P sorption at different P

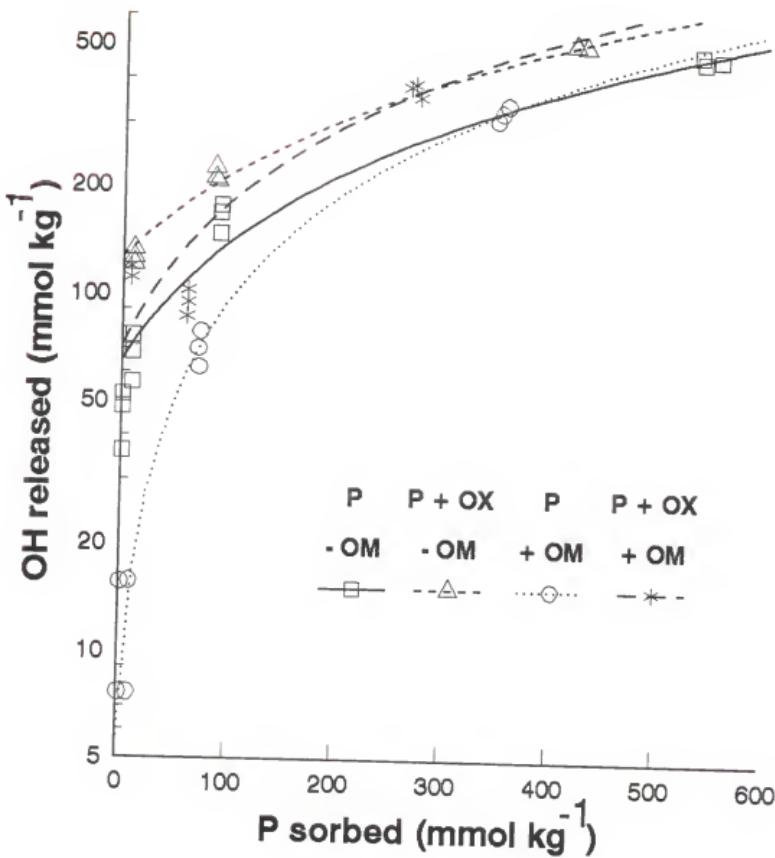


Fig. 3.3 Release of OH⁻ ions during sorption of P by the clay fractions.

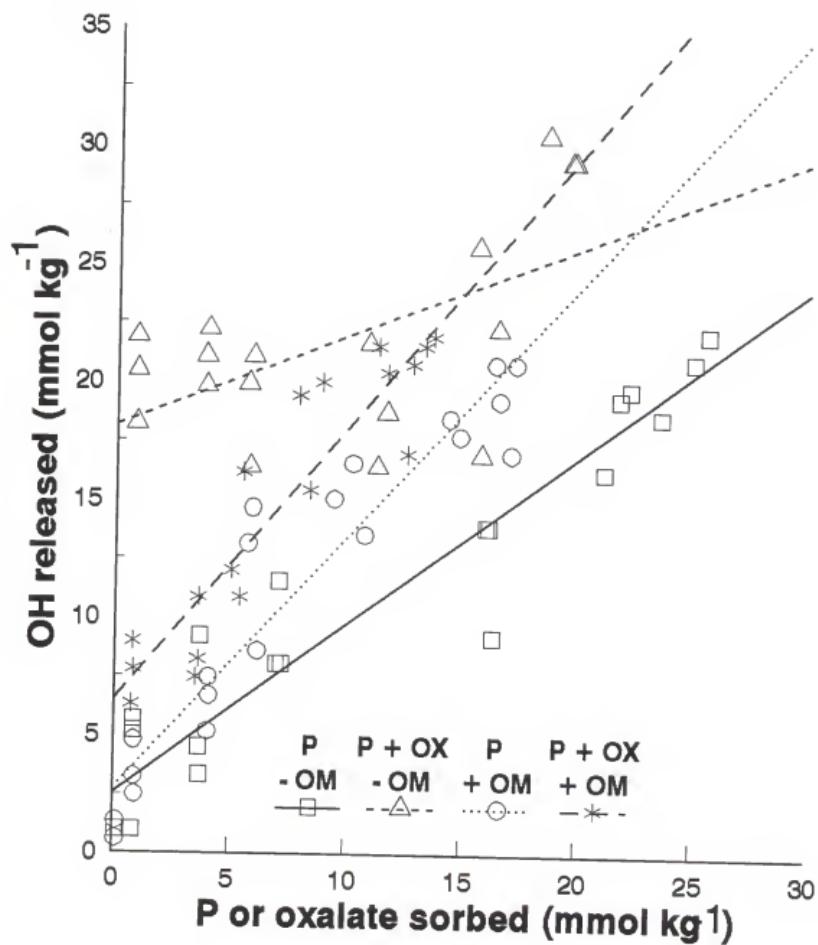


Fig. 3.4 Release of OH^- ions during sorption of P by the whole-soil samples.

Table 3.5. Parameters of the linear regression models for the release of OH⁻ ions and organic carbon from the whole-soil samples and clay fractions.

Treatments	OH ⁻ ions released			Organic Carbon released		
	Slope	Constant	R ²	Slope	Constant	R ²
Soil without organic matter						
P	0.66 ^a	2.9 ^a	0.89			
P + OX	0.59 ^a	16.1 ^b	0.80			
Soil with organic matter						
P	1.06 ^b	2.7 ^a	0.95	0.05 ^a	0.59 ^a	0.98
P + OX	1.19 ^b	5.8 ^a	0.94	0.06 ^a	0.71 ^a	0.94
Clay without organic matter						
P	0.74 ^a	66 ^b	0.99			
P + OX	0.91 ^b	116 ^c	0.99			
Clay with organic matter						
P	0.90 ^b	6 ^a	0.99	0.23 ^a	67.3 ^a	0.96
P + OX	1.08 ^c	72 ^b	0.96	0.22 ^a	128.8 ^b	0.98

Values within columns followed by the same letter for soil or clay samples are not significantly different at the 5% level

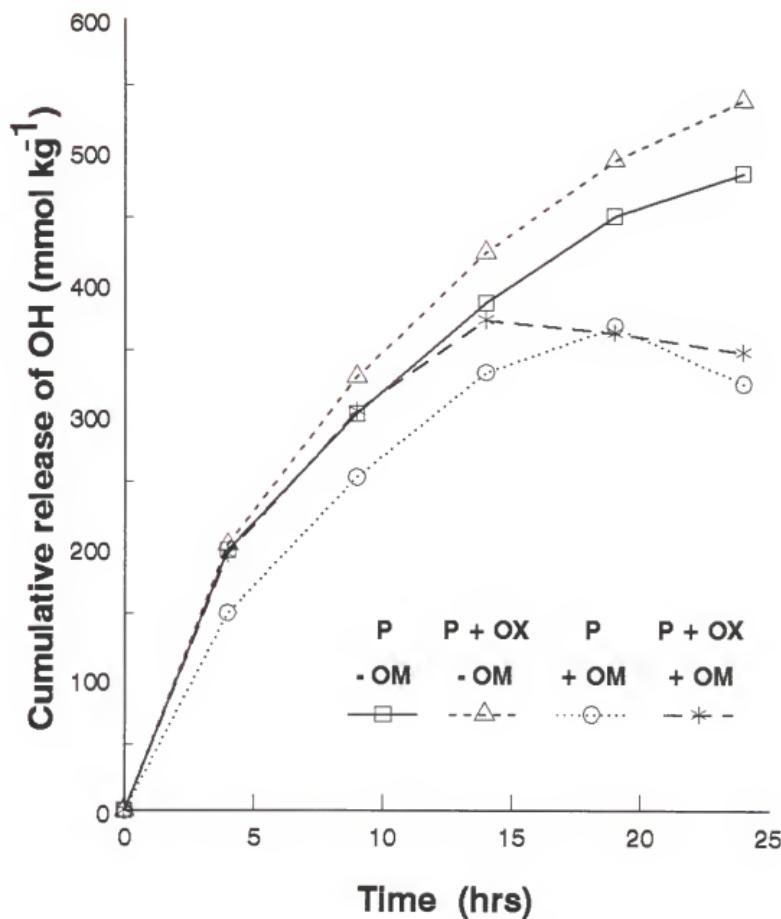


Fig. 3.5 Kinetics of OH^- release during sorption of anions by the clay fraction.

Table 3.6. Ratios of OH⁻ released to P sorbed for P only and P + oxalate for the whole-soil samples and the clay fractions (Mean \pm SD; n=3).

W/OM or WO/OM	Treatment	OH released/Anion sorbed	
		Whole soil	Clay fraction
With OM	P	*1.03 \pm 0.05 ^a	0.92 \pm 0.03 ^a
	P + Ox	1.61 \pm 0.10	1.38 \pm 0.08
Without OM	P	0.83 \pm 0.05 ^a	0.85 \pm 0.07 ^a
	P + Ox	1.53 \pm 0.08	1.24 \pm 0.11

Superscript "a" indicates that values are not significantly different from 1.0 at the 5% level.

loading rates (Table 3.7).

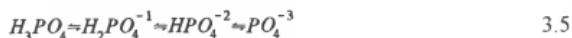
Release of Al and Fe.

A small amount of Al and Fe was released during the sorption of phosphate and for the P + oxalate sorption treatment, these amounts were even greater (Tables 3.3 and 3.8). Ion-activity product calculations using MINTQEA2 V3.11 showed that the system was supersaturated with respect to amorphous aluminum phosphate at the higher loading rates for P.

Discussion

The dissociation constants ($\log K_1$ and $\log K_2$) of oxalic acid are 1.27 and 4.20. At pH 4.5, both COOH groups of the oxalate will be dissociated, making the $C_2O_4^{2-}$ species dominant. Assuming ligand exchange as the surface reaction this oxalate species can form either monodentate, binuclear, or bidentate surface complexes.

The dissociation of phosphoric acid is described by:



where $pK_1 = 2.2$, $pK_2 = 7.2$ and $pK_3 = 12.3$. The predominant species of phosphate at pH 4.5 is $H_2PO_4^{1-}$. Thus, $H_2PO_4^{1-}$ should only form monodentate or binuclear surface complexes.

Table 3.7. E_4/E_6 ratio of organic carbon released into solution during the sorption of P only, and P + oxalate by the clay fractions (Means \pm SD; n=3).

Treatment	Concentration of Anions added (mM)	E_4/E_6 ratio
P	10	9.04 \pm 0.10 ^a
	1.0	9.31 \pm 0.25 ^a
	0.1	9.24 \pm 0.56 ^a
	0.0	9.26 \pm 0.07 ^a
P + Ox	10 + 1	9.14 \pm 0.06 ^a
	1.0 + 1	8.93 \pm 0.05 ^a
	0.1 + 1	7.65 \pm 0.21 ^b

Values within columns followed by same letter are not significantly different at the 5% level

Table 3.8 Parameters of the linear regression model relating release of aluminum and iron with P sorption for P only and P + oxalate by the whole-soil and clay fractions.

Treatments	Al release			Fe release		
	Slope	Constant	R ²	Slope	Constant	R ²
Soil with organic matter						
P	0.08 ^a	2.05 ^a	0.93	0.001 ^a	0.015 ^a	0.87
P + OX	0.01 ^a	7.66 ^b	0.07	0.0004 ^a	0.031 ^a	0.24
Soil without organic matter						
P	0.01 ^a	2.52 ^a	0.69	0.0001 ^a	-0.008 ^a	0.31
P + OX	-0.09 ^a	6.72 ^b	-0.94	-0.002 ^a	0.106 ^a	-0.84
Clay without organic matter						
P	0.03 ^a	34.27 ^a	0.94	0.0003 ^a	-0.01 ^a	0.97
P + OX	0.05 ^a	69.01 ^c	0.94	0.0005 ^a	-0.21 ^a	0.96
Clay With Organic Matter						
P	0.02 ^a	13.20 ^a	0.96	0.001 ^a	0.19 ^a	0.98
P + OX	-0.01 ^a	54.01 ^b	-0.61	0.001 ^a	0.52 ^b	0.97

Values within columns followed by the same letter for soil or clay samples are not significantly different at the 5 % level

P Sorption

Phosphate can be sorbed by the clay and whole-soil surfaces either by ligand exchange or precipitation. Ligand exchange should result in the release of OH⁻ ions into solution (Goldberg and Sposito, 1985). In fact, large amounts of OH⁻ were released in this study. The amount of OH⁻ ions released varied with the amount of P and/or of oxalate sorbed. The average ratio of OH⁻ released to phosphate sorbed was close to unity. When oxalate was also sorbed this ratio increased to 1.5. Given that the ratio was unity and that the dominant species of phosphate was the H₂PO₄⁻ ion, one could argue that P was forming a monodendate and/or binuclear inner-sphere complex. The ratio of OH⁻ ions released to P sorbed was similar for both the whole-soil and clay samples. Recently Tejedor-Tejedor and Anderson (1990) using CIR-FTIR studied the surface complexation of phosphate by goethite surfaces between pH 3.5 to 8.0. They suggested that between pH 3.5 and 5.5, phosphate formed both binuclear and monodendate complexes with surface Fe (III). Earlier work by Parfitt *et al.* (1977), using infrared spectroscopy, also reported the presence of both binuclear and monodendate surface complexes by P on goethite at pH 4.0.

The molar ratio of OH ions released to P sorbed supports ligand exchange as the dominant P sorption process onto both the clay and whole-soil samples. The formation of measureable crystalline aluminum phosphate was not possible, given the reaction time of this experiment. Veith and Sposito (1977) and Sposito (1984) reported that reaction times longer than 140 hrs are required for significant

discrete crystal growth to occur. This is much longer than the 24 hrs represented by this study. Sposito (1984) further suggested that the adsorption-dominated stage of phosphate sorption takes less than about 50 hrs. Calculated ion-activity product constants using MINTQEA2 V3.11 suggested that, at equilibrium, this system was supersaturated with respect to amorphous aluminum phosphate, $\text{Al(OH)}_2\text{H}_2\text{PO}_4$. The formation or precipitation of amorphous aluminum phosphate thus could be possible. Sorption of phosphate through ligand exchange is known to serve as a nucleation site for the precipitation of amorphous aluminum phosphate onto the clay surface. However, formation or precipitation of amorphous aluminum phosphate ($\text{Al(OH)}_2\text{H}_2\text{PO}_4$) consumes OH^- instead releasing them. Our kinetic data on the release of OH^- ions showed no evidence of this. Up to 14 hrs, OH^- ions were continuously released into the solution. This suggests a ligand-exchange reaction. After 14 hrs, there was no further release of OH^- ions into solution from the clay surfaces with organic matter present while the clay surfaces without organic matter were still releasing OH^- . Thus, for clay surfaces, there was no absolute decrease in OH^- concentration in solution. This suggests that precipitation of amorphous aluminum phosphate was unlikely. Therefore, these results suggest that ligand exchange was the dominant reaction for P sorption.

Effect of Oxalate and Organic Carbon on P Sorption

Phosphate sorption significantly decreased in the presence of oxalate. Likewise, P was effective in reducing oxalate sorption (Appendix B), indicating that

some of the sorption sites were common for either P or oxalate. These observations suggest that between 20 to 30 % of the sorption sites on the whole-soil material were common. Similar results were reported by other researchers. Competitive sorption studies for P and oxalate on tropical soils (Lopez-Hernandez et al., 1986) and montmorillonite (Kafkafi et al., 1988) showed that oxalate was effective in reducing P sorption. Each observed that oxalate masked about 20% of the sites otherwise available for P sorption.

Soil organic carbon significantly reduced P sorption capacity of both the clay and whole-soil samples. Only a small amount of organic carbon was released during P sorption, and the E_4/E_6 values for organic carbon released were high. E_4/E_6 ratios between 8 to 10 are generally indicative of fulvic acid, and ratios from 2 to 5 represent humic acid (Thurman, 1985). The E_4/E_6 ratio of released organic carbon following P sorption fit the range for fulvic acid and was similar to that for control samples. Since the ratio of OH released to P sorbed was close to 1 and the amount of organic carbon released into solution during P sorption was small. This suggests that P was not effective in replacing organic carbon sorbed onto the surfaces. The significant reduction in P sorption by mineral surfaces in the presence of organic matter indicates that organic carbon masked and/or occupied the active sites for P sorption. Characterization of the clay fractions using FTIR (Chapter 2) revealed the presence of -COOH surface groups associated with organic matter. Competitive sorption of soil organic matter and boron by soil material was studied by Marzadori *et al.* (1991). They observed that soil organic

matter appears to be responsible for occluding important adsorption sites on the surfaces of soil particles which otherwise would be available for boron sorption.

CHAPTER 4

INFLUENCE OF SOIL ORGANIC MATTER ON DESORPTION OF PHOSPHORUS AND OXALATE FROM A SPODIC HORIZON

Introduction

In Chapters 2 and 3, the sorption of oxalate and P by the clay fractions and the whole-soil material of a spodic horizon from northcentral Florida were studied. Phosphate and oxalate are specifically sorbed by replacing the coordinated -OH groups of Al present on the surfaces of oxides and clay minerals. As discussed in Chapter 3, oxalate reduced P sorption onto clay fraction and whole-soil surfaces. This investigation studied P and oxalate desorption from the clay fraction and the whole-soil material. Phosphorus sorbed to the soil surfaces can be taken up by plants after it has been desorbed into the soil solution.

The competitive sorption of organic anions and P on mineral surfaces has received attention because the presence of organic ligands in the rhizosphere is thought to influence P fixation and, therefore, the supply of P to the plant (Deb and Datta, 1967; Lopaz (1974); Appelt *et al.*, 1975; Earl *et al.*, 1979; Lopez-Hernandez *et al.*, 1986; Kafkafi *et al.*, 1988; Martell *et al.*, 1988; Fox *et al.*, 1990a; Fox *et al.*, 1990b; Violante *et al.*, 1991; Violante and Gianfreda, 1993). Oxalate in forest soils originates from exudates of plant roots and through the

activities of fungi and bacteria (Stevenson, 1982). Although oxalate is abundant in the rhizosphere (Fox and Comerford, 1990), only a few investigations have studied the competitive sorption of oxalate and phosphate. These include studies in tropical soils (Lopez-Hernandez *et al.*, 1986); and montmorillonite (Violante and Gianfreda, 1993). It has been proposed that oxalate can release P from Al- and Fe-hydroxide surfaces through ligand-exchange reactions. Recently, Fox *et al.* (1990a) studied the kinetics of P desorption by oxalate from spodic and argillic horizons of a Spodosol. They suggested that P released by oxalate was through ligand exchange, but did not provide conclusive evidence.

Phosphate desorption studies (Barrow, 1983; Kuo and Pan, 1988; Bakheit Said and Dakermanji, 1993; Raven and Hossner, 1993) have indicated that a large portion of the retained P is irreversibly sorbed. In all such desorption studies, researchers used either 0.01 M CaCl_2 , $\text{Ca}(\text{NO}_3)_2$ or anion exchange resins. Phosphate desorption isotherms do not normally coincide with P sorption isotherms (Nye and Tinker, 1977; Kuo and Pan, 1988; Bakheit Said and Dakermanji, 1993). Lopaz (1974) studied the desorption of P using citrate and found that desorption could only occur when the displacing anion was specifically sorbed and present in sufficient concentration in the soil solution. Organic anions like citrate and oxalate are continuously produced in soil (Smith, 1969) and can be present in high concentrations (Fox and Comerford, 1990). However, desorption isotherms using oxalate as an extractant have not been reported to our knowledge.

The influence of soil organic matter on P sorption has been investigated by many researchers. Many have suggested that sorption of P and organic matter occurs on the same sorption sites. Yuan (1980) studied the sorption of P and water-extractable soil organic matter by soil and Al oxides. He reported that most of the sorption sites for organic matter and P sorption may be different, though some sites are common for both P and organic matter. Fulvic acid was found to reduce P adsorption considerably. This effect of fulvic acid is apparently due to the chelating ability of fulvic acid's -COOH and -OH functional groups for Al and Fe (Parfitt, 1978; Sibanda and Young, 1986). The results in Chapter 3 showed that soil organic matter significantly reduced P sorption. However, the mechanism for P desorption in the presence of organic matter apparently has not be studied.

The objectives of this study were to investigate: i) P or oxalate desorption from the clay fraction and whole soil of a spodic horizon in the presence of oxalate or P, respectively, and ii) the influence of soil organic matter on the desorption of P and oxalate.

Materials and Methods

Whole-Soil Material and the Clay Fraction

The whole-soil and clay-fraction samples that were used for sorption studies of oxalate (Chapter 2) and phosphate (Chapter 3) were further used to study the desorption of anions at pH 4.5.

Phosphate Desorption by Oxalate

P sorption experiments described in chapter 3 formed the basis for these samples. In Chapter 3, the solutions used for P sorption by the clay samples had P concentrations of 0 mM, 0.1 mM, 1.0 mM, and 10 mM. The P sorption solutions used for the whole-soil samples had P concentrations of 0 mM, 0.1 mM, 0.5 mM, 1.0 mM, 3.0 mM, 7.0 mM and 10 mM. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. Filtrates then were equilibrated with solution containing 5 mM of oxalate per 25 ml of solution for the clay fractions and per 50 ml of solution for the whole-soil samples. The suspensions were then shaken for another 24 hrs. The suspension pH was periodically (every four hours) adjusted to pH 4.5 with 0.1 M HCl or NaOH over the 24 hrs of the experiment. Two drops of toluene were added to inhibit microbial growth, and samples were placed in a reciprocating shaker for 24 hrs. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. The filtrate then was analyzed for oxalate, Al, Fe, inorganic P and organic carbon. Sorbed oxalate was calculated from the difference between the initial and final oxalate concentration in solution.

Oxalate Desorption by Phosphate

The oxalate sorption experiments of Chapter 2 served as the basis for these samples. The solutions used for the initial sorption of oxalate in Chapter 2 had oxalate concentrations of 0 mM, 0.1 mM, 1.0 mM, and 10 mM for the clay

fractions. Oxalate concentrations used for the whole-soil sorption isotherms were 0 mM, 0.1 mM, 0.5 mM, 1.0 mM, 3.0 mM, 7.0 mM and 10.0 mM. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. Filtrates then were equilibrated with 25 ml of a 5 mM P solution for the clay fraction or with 50 ml of solution for the whole-soil samples. The suspension then was shaken for another 24 hrs. pH of the suspension was periodically (every four hours) adjusted to pH 4.5 with 0.1 M HCl or NaOH over the 24 hrs of the experiment. Two drops of toluene were added to inhibit microbial growth, and samples were placed in a reciprocating shaker for 24 hrs. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. The filtrate was used for analysis of oxalate, Al, Fe, inorganic P and organic carbon. Sorbed phosphate was calculated from the difference between the initial and final phosphate solution concentrations.

Chemical Analysis

Solution pH was measured using a combination glass electrode on an Orion pH meter. Aluminum was determined using a flame emission spectrophotometer with $N_2O-C_2H_2$ flame, and Fe was determined using a C_2H_2 flame. Total organic carbon of the clay suspension with organic matter was measured using a persulfate oxidation followed by IR analysis of the CO_2 produced on a TOC apparatus (College Station, TX).

Oxalate in the extract was determined by HPLC (Fox and Comerford, 1990a), using a Hamilton PRP-X300 150 x 4.1 mm organic acid column (Hamilton Co., Reno, Nevada) with a Gilson single piston high pressure pump along with a Rheodyne model 7125 injection valve fitted with a 20 μL injection loop. This HPLC system uses a Gilson Holochrom variable wavelength UV detector in conjunction with a Gilson computerized integrator. The eluent was 0.005 M H_2SO_4 at a flow rate of 2 mL min^{-1} . Oxalate concentration was calculated from a calibration curve obtained with standard solutions of 0.1 to 10 mM.

To determine the amount of OH^- released with the sorption of oxalate, titration curves were prepared for the whole-soil and clay fractions samples (with and without organic matter) as described in Chapter 3. Models were fitted to these curves and used to calculate the changes in OH concentration required to change the pH of the system to specific values.

Adsorption Isotherms

Freundlich model was fitted to the desorption data. The Freundlich model was obtained by:

$$S = kC^{\frac{1}{n}} \quad (4.1)$$

where S and C are defined as previously and k and n are empirical constants.

The linear form of the above equation was used to determine sorption parameters.

Speciation Calculations

The metal speciation model MINTEQA2 version 3.2 was used to calculate the species of Al, P and oxalate in the solution. It was assumed that the system had achieved equilibrium conditions. Log K values for Al-oxalate complexes were obtained from Thomas *et al.* (1991). Assigned Log K values were 6.12 for $\text{AlC}_2\text{O}_4^{+1}$ and 11.15 for $\text{Al}(\text{C}_2\text{O}_4)_2^-$. The formation constants used for calculations of other species were those of the MINTEQA2 data base, as taken from Martell and Smith (1982).

Statistical Analysis

Statistical differences in desorption of oxalate or phosphate using different regression lines were tested using the General Linear Models procedure of the SAS framework (SAS Institute, 1985). Observed desorption of oxalate or phosphate was related to the amount of P and oxalate previously present on the surfaces, respectively. The model employed was:

$$Y = \alpha + \beta_1(\log Y_{ij}) + \beta_2(\log X_{ij})^2 + \epsilon_{ij} \quad (4.2)$$

where α is the intercept, β_1 and β_2 are 1st and 2nd order coefficients of the line and ϵ is the error term. To compare two regression lines, we compared the α and β values of the two lines with ANOVA and t-test used to test the differences between α_1 and α_2 as well as between β_1 and β_2 . The significance of the

difference between means was determined by a t-test (Snedecor and Cochran, 1980). Standard deviations or standard errors of means are given as appropriate.

Results

Desorption of Phosphate in the Presence of Oxalate

Desorption of Phosphate

A considerable amount of phosphate was desorbed during oxalate sorption, and the presence of organic matter did not significantly influence the desorption of P by oxalate. P desorption isotherms are presented in Figure 4.1 both for the clay fractions and the whole-soil samples. Corresponding parameters for the Freundlich models are presented in Table 4.1.

Sorption of Oxalate

Oxalate sorption by the clay fraction and the whole-soil samples is presented in Figure 4.2 and 4.3, respectively. The amount of oxalate sorbed increased as the amount of P previously present on the mineral surfaces decreased both for the whole soil and the corresponding clay fractions. The relationship between release of previously sorbed P and amount of oxalate sorbed is presented in Appendix D-1. As low amounts of oxalate were sorbed in the present experiment, large amounts of P were desorbed. The amount of oxalate sorption followed a quadratic model. Parameters of the model are presented in Table 4.2. The amount of oxalate

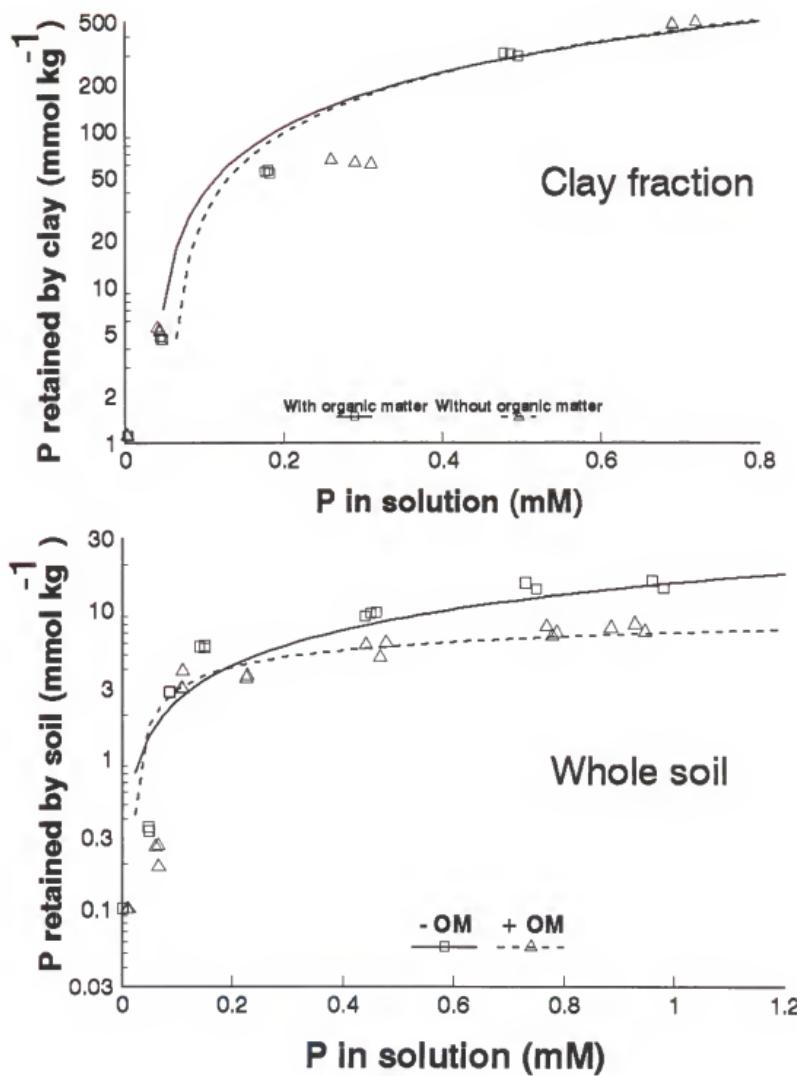


Fig. 4.1 P desorption curves for whole-soil samples and clay fraction.

Table 4.1. Parameters of Freundlich models for the desorption of P from whole-soil samples and clay fraction in the presence of 5 mM oxalate.

Type of Surfaces	Desorption Constant K	Bonding Energy N	R ²
<u>Whole Soil</u>			
With Organic matter	10.59 ^a	0.98 ^a	0.85
Without Organic matter	18.08 ^a	1.23 ^a	0.86
<u>Clay Fractions</u>			
With organic matter	354 ^a	0.94 ^a	0.91
Without organic matter	301 ^a	1.03 ^a	0.90

Letters in column are significantly different at the 5% level for clay and soil materials.

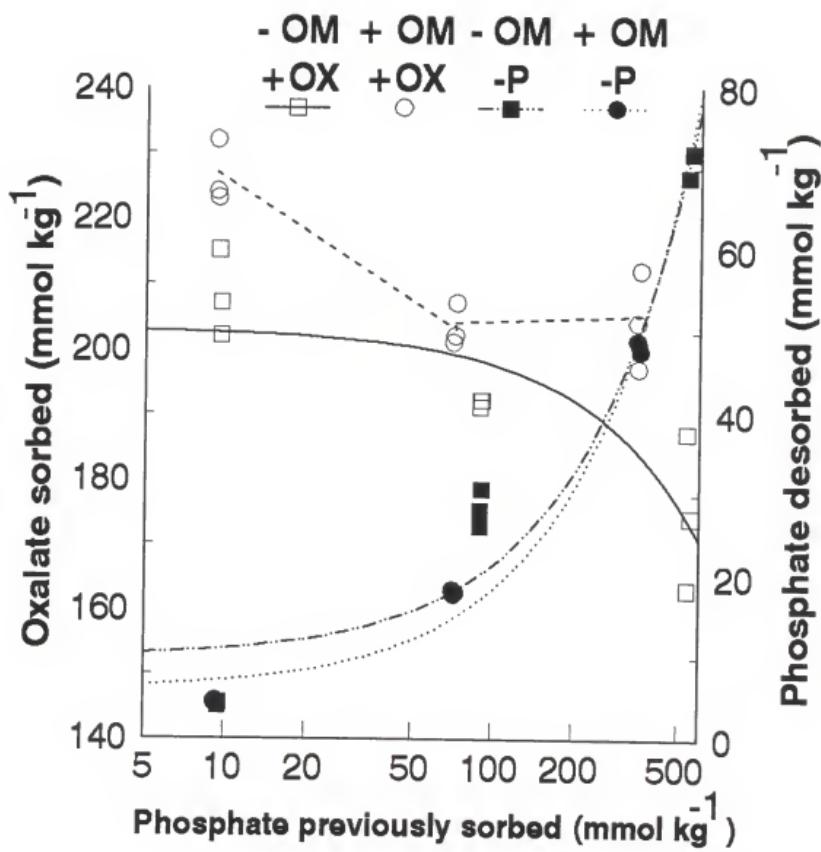


Fig. 4.2 Influence of previously sorbed P on oxalate sorption and P desorption for clay fraction.

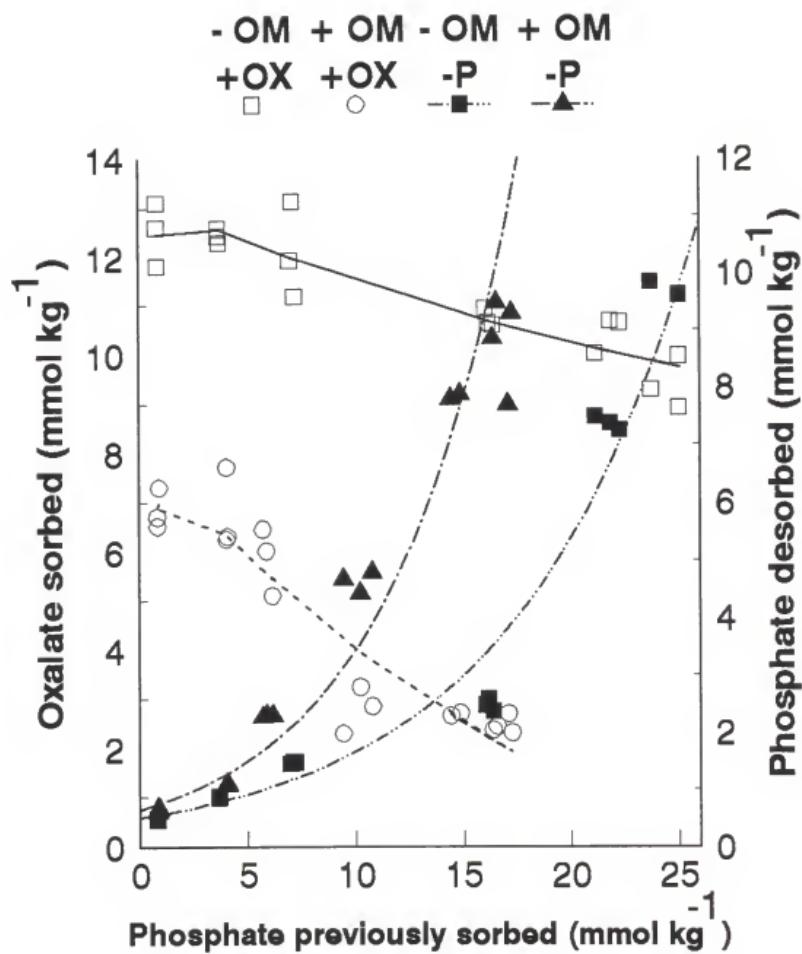


Fig. 4.3 Influence of previously sorbed P on oxalate sorption and P desorption by whole-soil samples.

Table 4.2. Quadratic equation coefficients for the sorption of anions by whole-soil samples and clay fractions.

Anion Sorbed	Materials	α	β_1	β_2	R^2
OX	Clay + OM ^a	160	76.5	-39.4	0.94
	Clay - OM ^b	378	-24.9	2.8	0.95
	Soil + OM ^a	11.4	5.63	-10.7	0.92
	Soil - OM ^b	14.5	3.67	-7.66	0.97
P	Clay + OM ^a	283	-76.6	17.5	0.85
	Clay - OM ^b	213	-3.89	-3.7	0.74
	Soil + OM ^a	7.1	1.74	-4.76	0.87
	Soil - OM ^b	12.6	1.32	-2.41	0.82

+ OM= With organic matter and - OM = Without organic matter.

Different letters in the same column are significantly different at the 5% level for the clay and soil samples.

sorption was significantly higher for materials without organic matter than with organic matter.

Release of Hydroxyls

Hydroxyls were released into solution during the sorption of oxalate by both the whole-soil and clay fraction (Appendix D-1). The ratios of OH⁻ desorbed to the amount of oxalate sorbed and are presented in Table 4.3. This ratio ranged between 1.68 and 1.90 for the clay fraction and between 1.64 and 2.01 for the whole-soil samples. The ratio of OH⁻ desorbed to oxalate sorbed increased as the amount of P desorbed in solution decreased.

For the clay fraction, ratios of OH⁻ + P released into solution to oxalate sorbed were not significantly different from 2. Ratio was significantly higher than 2 for the whole-soil samples, however, with higher amounts of P previously present on these surfaces.

Release of Al, Fe, and Organic Carbon

Considerable amounts of aluminum, iron and organic carbon were released into the solution during oxalate sorption, both for the whole-soil samples and the clay (Appendix D-1). There was a significant correlation between the amounts of Al and Fe released and oxalate sorbed.

Table 4.3 Influence of oxalate sorption by clay fractions and whole-soil samples on the ratio of OH released, and OH + P released, to oxalate sorbed (Mean \pm SD; n=3).

Without Organic Matter			With Organic Matter		
P Prev. Present (mmol kg ⁻¹)	Ratio		P Prev. Sorbed (mmol kg ⁻¹)	Ratio	
	OH/OX	(OH + P)/OX		OH/OX	(OH + P)/OX
<u>Clay fraction</u>					
545 \pm 9	1.87 \pm 0.1 ^{aa}	2.12 \pm 0.1 ^{ab}	353 \pm 5	1.68 \pm 0.1 ^{aa}	1.92 \pm 0.1 ^{ab}
91 \pm 0.3	1.86 \pm 0.1 ^{aa}	2.05 \pm 0.1 ^{aa}	72 \pm 1	1.83 \pm 0.1 ^{aa}	1.96 \pm 0.06 ^{aa}
9.5 \pm 0.5	1.90 \pm 0.1 ^{aa}	1.91 \pm 0.1 ^{aa}	9 \pm 1	1.89 \pm 0.0 ^{aa}	1.85 \pm 0.10 ^{aa}
<u>Whole Soil Material</u>					
24.5 \pm 0.7	1.64 \pm 0.1 ^{aa}	3.22 \pm 0.2 ^{ab}	16.7 \pm 0.5	1.75 \pm 0.1 ^{aa}	4.21 \pm 0.2 ^{ab}
21.7 \pm 0.6	1.73 \pm 0.1 ^{aa}	3.11 \pm 0.1 ^{ab}	15.5 \pm 1.4	1.79 \pm 0.1 ^{aa}	3.14 \pm 0.2 ^{bb}
16.2 \pm 0.2	1.76 \pm 0.1 ^{aa}	3.04 \pm 0.2 ^{ab}	10.2 \pm 0.7	1.84 \pm 0.1 ^{aa}	2.83 \pm 0.1 ^{bb}
7.1 \pm 0.1	1.69 \pm 0.1 ^{aa}	2.16 \pm 0.1 ^{bb}	5.4 \pm 0.2	1.81 \pm 0.2 ^{aa}	2.45 \pm 0.4 ^{ab}
3.7 \pm 0.1	1.83 \pm 0.1 ^{ab}	2.06 \pm 0.1 ^{ba}	4.1 \pm 0.1	1.85 \pm 0.1 ^{aa}	2.32 \pm 0.3 ^{ca}
0.8 \pm 0.1	2.01 \pm 0.1 ^{ba}	1.93 \pm 0.1 ^{ba}	0.9 \pm 0.1	1.85 \pm 0.1 ^{aa}	1.88 \pm 0.1 ^{ca}

The first superscript letter indicates significant differences within a column and material, while the second letter indicates significant differences between rows.

Desorption of Oxalate in the Presence of Phosphate

Desorption of Oxalate and Sorption of Phosphate

Small amounts of oxalate were desorbed by the whole-soil samples and the clay fraction with the sorption of phosphate (Figs. 4.4 & 4.5). Higher amounts of oxalate were released from the soil and clay containing organic matter. The sorption of P by clay and soil surfaces is presented in Figures 4.4 and 4.5. The presence of previously sorbed oxalate onto the clay surface had no significant influence on P sorption in the present experiment.

Release of Hydroxyls

The amounts of hydroxyl released to solution during P sorption are presented in Appendix D-2. The ratio of OH⁻ released to amount of P sorbed was calculated and shown to vary between 0.89 and 1.08 for the clay fractions and between 0.85 to 1.15 for Values were not significantly different from 1 (Table 4.4), and ratios were not influenced by the amount of oxalate desorbed into solution.

The ratio of OH + Ox released into solution to P sorbed was also calculated (Table 4.4). The two ratios (OH/P and (OH + Ox)/P) were not significantly different for the clay samples. However, at high amounts of oxalate previously present on whole-soil surfaces, OH + Ox/ P ratio were significantly greater than 1.

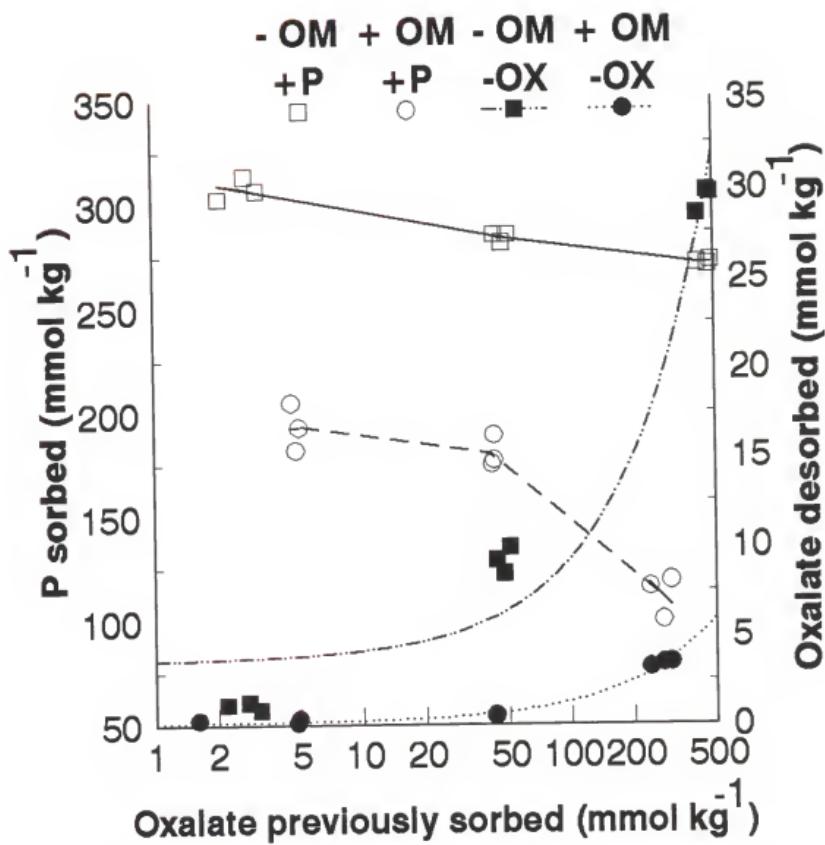


Fig. 4.4 Influence of previously sorbed oxalate on P sorption and oxalate desorption for clay fraction.

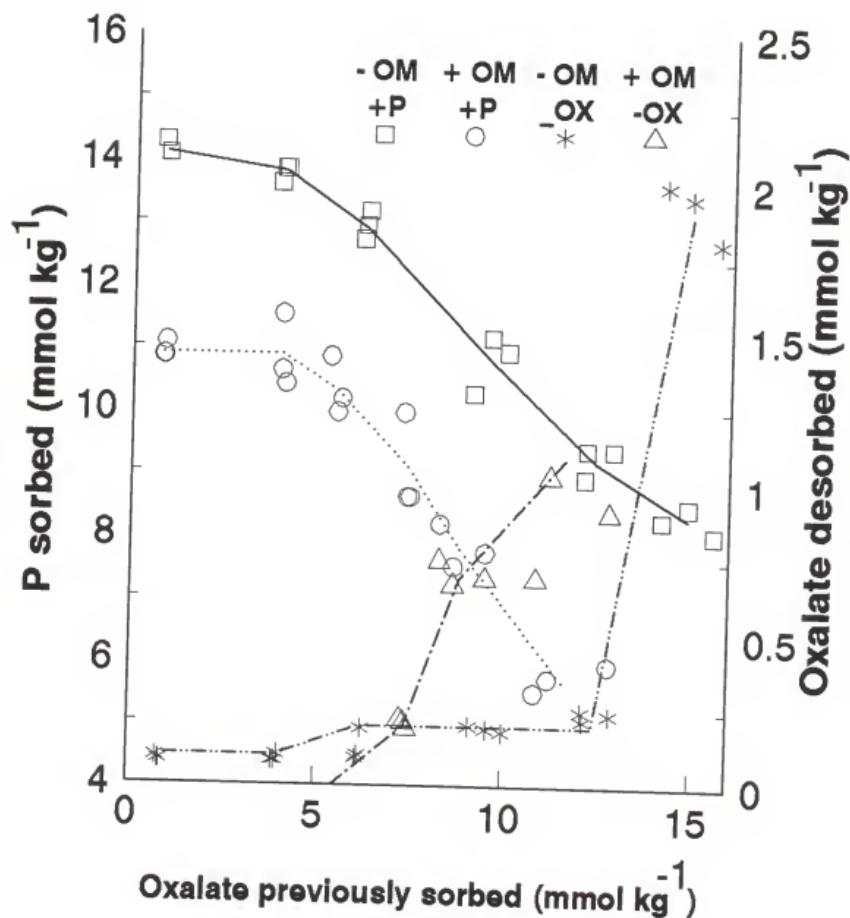


Fig. 4.5. Influence of previously sorbed oxalate on P sorption and oxalate desorption by whole-soil samples.

Table 4.4 Influence of P sorption by clay fractions and whole-soil samples on the ratio of OH released, and OH + oxalate released, to P sorbed (Mean \pm SD; n=3).

Without Organic Matter			With Organic Matter		
Ox Prev [^] Present (mmol kg ⁻¹)	Ratio OH/P	(OH + Ox)/P	Ox Prev. Present (mmol kg ⁻¹)	Ratio OH/P	(OH + Ox)/P
<u>Clay Fractions</u>					
456 \pm 17	0.94 \pm 0.1 ^{aa}	1.04 \pm 0.1 ^{aa}	275 \pm 14	0.89 \pm 0.1 ^{aa}	0.92 \pm 0.1 ^{aa}
48 \pm 2.4	1.08 \pm 0.1 ^{aa}	1.03 \pm 0.1 ^{aa}	43 \pm 0.2	0.98 \pm 0.1 ^{aa}	0.98 \pm 0.1 ^{aa}
3 \pm 0.5	0.98 \pm 0.1 ^{aa}	0.99 \pm 0.1 ^{aa}	5 \pm 0.2	0.95 \pm 0.1 ^{aa}	0.95 \pm 0.1 ^{aa}
<u>Whole Soil Material</u>					
14.9 \pm 0.7	1.08 \pm 0.1 ^{aa}	2.99 \pm 0.2 ^{ab}	11.6 \pm 1.0	1.03 \pm 0.1 ^{aa}	2.90 \pm 0.3 ^{ab}
12.4 \pm 0.4	1.01 \pm 0.1 ^{aa}	1.25 \pm 0.2 ^{ba}	8.8 \pm 0.6	1.09 \pm 0.2 ^{aa}	2.05 \pm 0.2 ^{bb}
9.6 \pm 0.5	1.15 \pm 0.1 ^{aa}	1.35 \pm 0.2 ^{ba}	7.4 \pm 0.1	1.06 \pm 0.1 ^{aa}	1.26 \pm 0.2 ^{ca}
6.2 \pm 0.7	0.96 \pm 0.1 ^{aa}	1.16 \pm 0.2 ^{ba}	5.5 \pm 0.2	1.07 \pm 0.1 ^{aa}	1.07 \pm 0.1 ^{ca}
4.0 \pm 0.1	0.85 \pm 0.1 ^{aa}	0.99 \pm 0.1 ^{ba}	4.0 \pm 0.1	0.98 \pm 0.1 ^{aa}	0.98 \pm 0.1 ^{ca}
0.8 \pm 0.1	0.99 \pm 0.1 ^{aa}	1.04 \pm 0.1 ^{ba}	0.8 \pm 0.1	1.04 \pm 0.1 ^{aa}	1.04 \pm 0.1 ^{ca}

[^]Ox Prev is Oxalate previously sorbed;

The first superscript letter indicates significant differences within a column and material, and the second letter indicates significant differences between rows.

Release of Al, Fe, and Organic Carbon

Small amounts of Al, Fe and organic carbon were released into solution during P sorption. The amounts of Al and Fe desorbed by clay and soil with and without organic matter are presented in Appendix D-2. The amounts of Al and Fe released to solution were higher for the clay fraction and for the whole-soil samples having organic matter.

Discussion

Phosphate Desorption by Oxalate

It has been previously shown that i) oxalate and P are retained on surfaces of clay particles and whole-soil samples through ligand exchange (Chapter 2; Chapter 3; Parfitt *et al.*, 1977; Sposito, 1984; Goldberg and Sposito, 1985); ii) oxalate sorption causes dissolution of the mineral surfaces (Chapter 2; Stumm, 1986); and iii) at pH 4.5, oxalate formed a bidentate surface complex (Chapter 2) while P was sorbed as monodentate and/or binuclear surface complexes (Chapter 3).

We postulated that oxalate released P from the mineral surfaces through two processes: i) ligand exchange replacing P from the mineral surfaces; and ii) dissolution of the mineral surfaces and release of P into solution.

The data indicated that, when high amounts of P were present on the mineral surfaces, P was released into solution during oxalate sorption. At pH 4.5, oxalate would form bidentate complexes with the mineral surface and the ratio

of OH released to oxalate sorbed would be 2 (Chapter 2). If oxalate sorption released previously-sorbed P into solution through ligand exchange, than one would not expect the ratio of OH⁻ released to oxalate sorbed to be close to 2. Data from this study support this observation. The ratio of OH⁻ released to oxalate sorbed was significantly less than 2 when higher amounts of P were present on the surfaces. However, the ratio of OH⁻ + P released into solution to oxalate sorbed is equal to 2 for the clay fraction samples. This confirmed that oxalate released some P directly through ligand exchange, with some sites for P and oxalate sorption being common.

For whole-soil samples, the ratio of OH⁻ + P released to oxalate sorbed was significantly higher than 2 when higher amounts of P were present on the surfaces. The higher ratio suggests that more P was desorbed into the solution with each unit of oxalate sorbed. A second process which can bring P into solution is dissolution of the soil surfaces. Release of Al and desorption of P each support the observation that oxalate sorption caused some surface dissolution. Oxalate dissolution of mineral surfaces was also observed in earlier studies (Chapter 2; Stumm, 1986). Therefore, one can argue that some P also was released into the soil solution through the dissolution of mineral surfaces.

Once P was released into solution along with Al, it could form various solution species as AlH₂PO₄(OH)₂ and AlH₂PO₄C₂O₄, or reprecipitate as amorphous aluminum phosphate. For P to reprecipitate on the mineral surfaces, soluble species of aluminum phosphate should first form in solution. This would serve as

nuclei for subsequent precipitation. However, the log K of soluble aluminum phosphate species in solution ($\text{AlH}_2\text{PO}_4(\text{OH})_2$ log K =3.0) is low compared those to the possible aluminum oxalate species in solution $[\text{AlC}_2\text{O}_4^+ (6.5)$ or $\text{Al}(\text{C}_2\text{O}_4)_2^- (13.7)$]. Therefore, oxalate should form stable soluble complexes with Al as AlC_2O_4^+ or $\text{Al}(\text{C}_2\text{O}_4)^-$. The speciation calculations also suggested that less than 10% of the P in solution was present as aluminum oxalate phosphate complexes ($\text{AlH}_2\text{PO}_4\text{C}_2\text{O}_4$), with the majority of the P being in the form of H_2PO_4^- species. Thus, one would expect P desorbed into solution by oxalate to be in the H_2PO_4^- form.

Oxalate Desorption by Phosphate

The small amount of oxalate that was desorbed by P indicates that oxalate ions were held very strongly by the clay particle and whole-soil surfaces. Oxalate forms bidentate surface complexes (Chapter 2, Parfitt *et al.*, 1977). P forms monodentate or binuclear complexes (Chapter 3; Parfitt, 1978; Tejador Tejador and Anderson, 1990). Since oxalate forms a stronger complex, P could not replace the sorbed oxalate. Our data suggest that the ratio of OH^- released to P sorbed by the whole-soil samples and the clay fractions in this study was not significantly different from unity. This confirmed that P was sorbed onto the clay fractions and whole-soil surfaces as monodentate and/or binuclear surface complexes, and that P was sorbed by sites on the clay and soil surfaces not already occupied by oxalate.

As P sorption was not affected by the presence of previously sorbed oxalate, one can conclude that many sites are highly specific for P.

Conclusions

This investigation elucidate the mechanism of P and oxalate desorption from spodic horizon materials. Results from this study confirmed that oxalate released P from the mineral surfaces through two processes: i) ligand exchange replacing P from the mineral surfaces; and ii) dissolving the mineral surface, thereby bringing sorbed P into solution. Results from the preceding chapter and this study establish that the presence of soil organic matter and oxalate increases the amount of P desorbed. Soil organic matter and oxalate significantly increase the P concentration in solution.

CHAPTER 5

CONCLUSIONS

Following are the major conclusions from this research, its significance with respect to the P nutrition of plants, and an outline of priorities for future studies.

Conclusions from this Study

Oxalate Sorption

1. Oxalate was sorbed by the clay fractions and whole-soil samples through ligand exchange.
2. Sample pH determined the charge characteristics of clay surfaces and the species of oxalate in solution, which in turn controlled the sorption process. Oxalate formed monodentate and/or binuclear complexes at pH 3.5, while bidentate surface complexes were formed at pH 4.5 and 5.5.
3. Soil organic matter significantly reduced the amount of oxalate sorbed by the mineral surfaces.
4. Data from this study provided experimental evidence for the theory of congruent dissolution as proposed by Stumm (1986). Sorption is the first step in the dissolution of mineral surfaces. Through sorption, oxalate forms

a coordinated complex with Al at the mineral surface, with sufficient strength to break the Al-O bond and solubilize the metals into solution.

5. Considerable amounts of organic carbon were released into solution during the sorption of oxalate. Aluminum ions can form cation bridges between the soil organic carbon and soil particles. Oxalate can detach this bridge to form soluble complexes with Al in solution, resulting in the release of large amounts of organic carbon.
6. The organic carbon released into solution during oxalate sorption had a lower E_4 to E_6 ratio, suggesting that it was humic in nature.

P Sorption

7. P appeared to be sorbed by the mineral surfaces through a ligand-exchange process. P formed monodendate and/or binuclear complexes on the mineral surfaces.
8. Organic carbon reduced P sorption. Maximum reduction in P sorption (about 50 %) was observed when both organic carbon and oxalate were present.
9. Some of the sites for sorption onto the surfaces of soil and clay particles were common for oxalate, P and organic carbon.
10. P sorption released small amounts of Al, Fe and organic carbon into solution.

P and Oxalate desorption

11. P desorption from the spodic horizon by oxalate appeared to be through two processes: i) ligand exchange replacing P from the mineral surfaces; and ii) oxalate forming surface complexes through ligand exchange (replacing OH ions), dissolving the mineral surfaces, and releasing P into solution.
12. Soil organic matter and oxalate significantly increased P desorption.
13. Once P was released into solution, oxalate did not allow P to reprecipitate by forming stable and soluble complexes with Al and Fe.
14. Oxalate was not released into the solution from spodic horizon material during P sorption.
15. Some of the sites were highly specific for P sorption.

Influence of Oxalate on the P Nutrition of Trees

P availability often limits forest productivity in flatwood soils. These results provide information about the availability of P in a spodic horizon.

Phosphorus is absorbed by plants largely as soluble $H_2PO_4^-$ or HPO_4^{2-} species. A soil's ability to supply P is determined by the concentration of P in the soil solution, along with its ability to replenish any P lost from solution. Our results confirm that oxalate significantly increases the solution concentration of P by: i) reducing P sorption; ii) releasing P into solution from sorbed and insoluble pools; and iii) complexing Al, Fe or Ca in solution, thereby reducing

P precipitation. This could increase the initial P concentration in solution and affect the P buffer power of these soils resulting in a higher concentration of P in solution.

The oxalate concentration in the rhizosphere of a spodic horizon range from 0.0 to 2.8 mM (Fox and Comerford, 1990). This reported concentration of oxalate in bulk soil solution tends to be much lower then in the vicinity of roots and fungal hyphae. It seems reasonable to assume that actual concentration near roots may be one or two orders of magnitude higher than the concentration in bulk soil solution. The oxalate concentration of 5 mM used in this study to desorb P exists under field conditions. At this oxalate concentration, the whole-soil samples released 0.1 mM P into solution.

Assuming a gravimetric moisture content of 20 % and a 0.1 mM concentration of P, the total amount of P in the soil solution at one time would be 0.6 mg kg⁻¹. However, slash pine roots occupy less than 1 % of the soil volume (Van Rees and Comerford, 1986). Therefore, high concentrations of oxalate would exist in the zone immediately adjacent to the roots, which is only a few millimeters wide and coincides with the rhizosphere region where microorganism are particularly active. To include the influence of fungal hyphae along with roots, one can further assume that these high concentration of P (0.6 mg kg⁻¹) would be present in approximately 2 % of soil volume. Assuming that the entire pool of oxalate was being replenished on a weekly basis (Fox *et al.*, 1990b), the spodic horizon would contribute approximately 0.6 kg P ha⁻¹yr⁻¹ to

the trees. Using $\text{Ca}(\text{NO}_3)_2$ as a extractant instead, the estimated contribution is approximately 0.20 kg of P $\text{ha}^{-1}\text{yr}^{-1}$. As pine trees remove roughly 3 kg P $\text{ha}^{-1}\text{yr}^{-1}$ from the soil, this is about 20 % of the tree's demand. Given this example, it shows that oxalate could significantly increase the availability of P in spodic-horizon material. These results, in combination with earlier work (Fox *et al.*, 1990a; Fox *et al.*, 1990b; Neary *et al.*, 1990) highlight the potential importance of subsoil fertility to the productivity of pine plantations in flatwoods.

Future Research

Results from this study have defined the mechanism of P release into the soil solution by oxalate, and its influence on initial solution P concentrations and buffer power for this soil. The next step could be to incorporate this information into a mechanistic nutrient uptake model in order to predict P uptake by plants. This should support the conclusion that oxalate released into the soil solution increases P availability in these soils.

To enhance our understanding of P cycling in spodic horizons, further work should address the following issues:

1. Influence of oxalate on P sorption and desorption in the presence of additional cations and anions.
2. Identification and characterization of organic P compounds.

3. Since oxalate significantly influenced the sorption and desorption of inorganic P, its influence on the sorption and desorption reactions of organic P compounds also needed to be investigated.
4. Characterization of the organic carbon released into solution, using NMR and FTIR techniques to understand its nature and influence on nutrient availability.

APPENDIX A

TITRATION CURVES FOR THE CLAY FRACTION AND WHOLE-SOIL MATERIAL

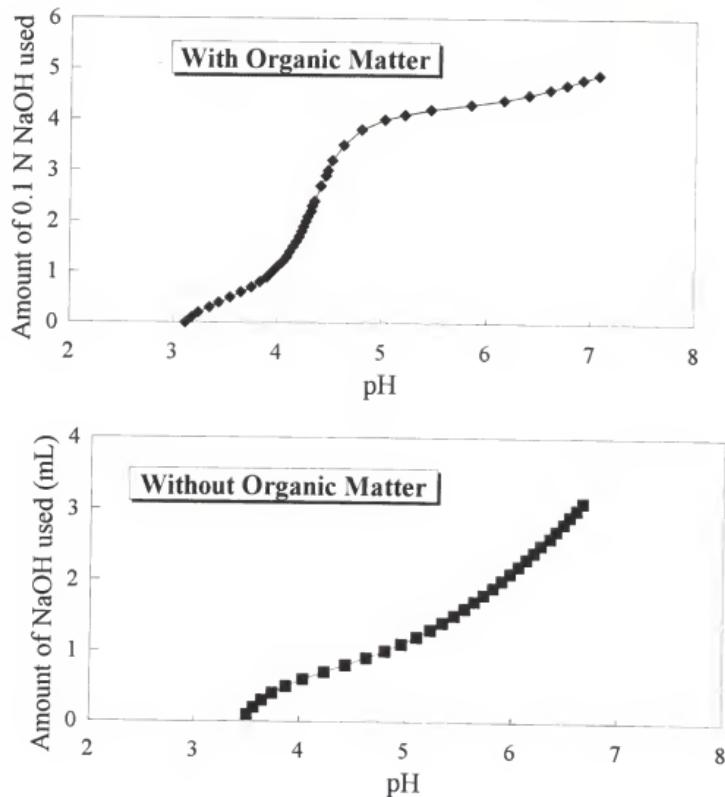


Fig. A-1 Titration curves for the clay fraction: A) With organic matter, B) Without organic matter.

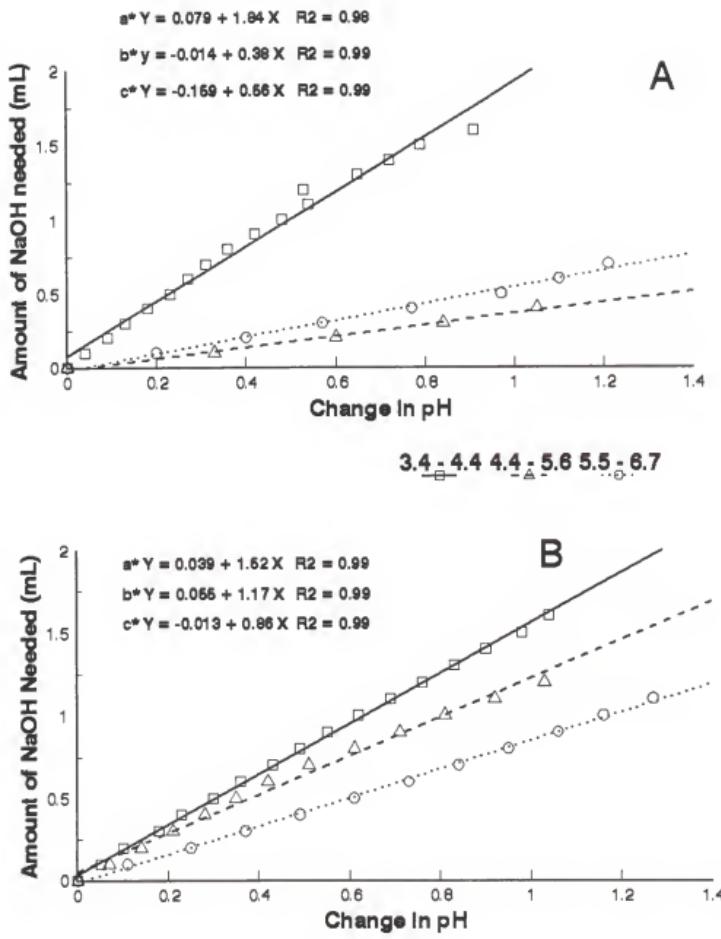


Fig. A-2 Buffer curves for the clay fraction, used to calculate the amount of OH⁻ released into solution: A) With organic matter, B) Without organic matter.

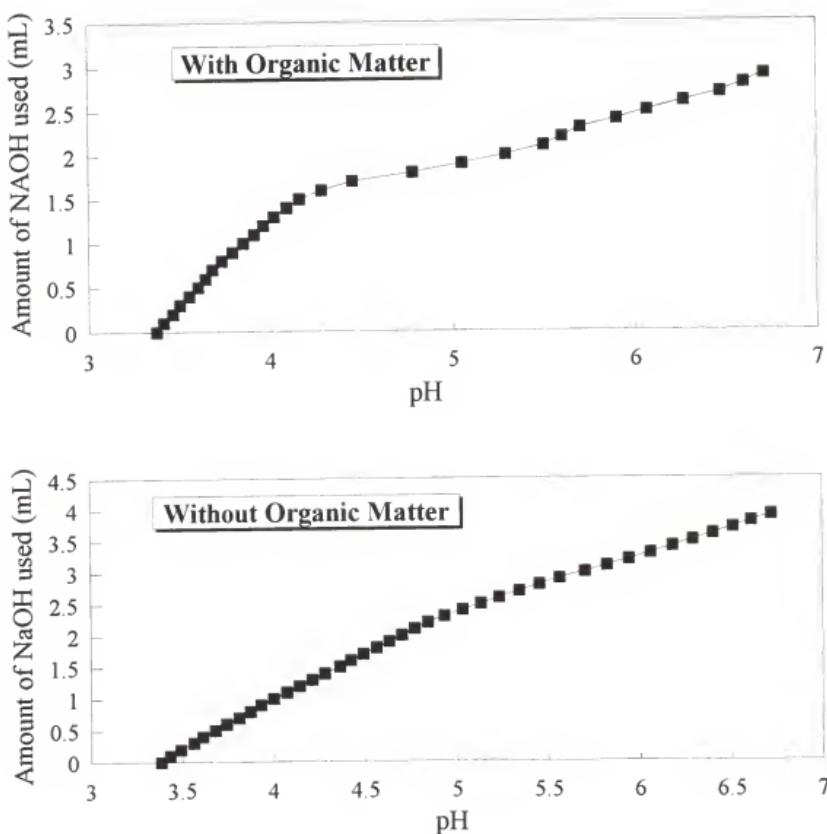


Fig. A-3. Titration curves for the whole-soil: A) With organic matter, B) Without organic matter.

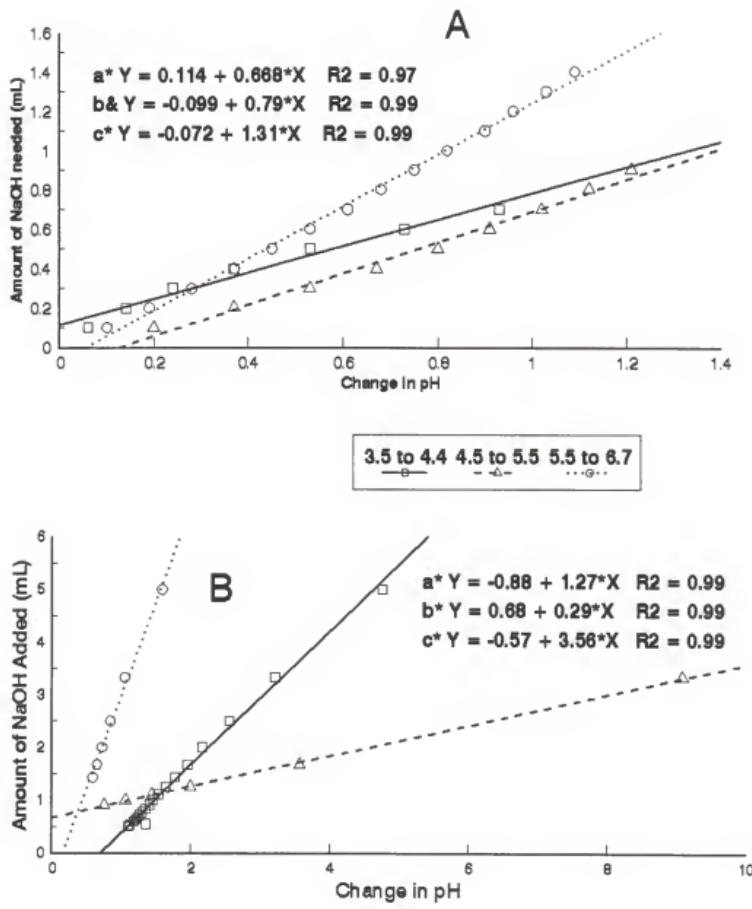


Fig. A-4 Buffer curves for the whole-soil, used to calculate the amount of OH^- released into solution: A) With organic matter, B) Without organic matter.

APPENDIX B

SORPTION OF OXALATE IN THE PRESENCE OF PHOSPHATE ONTO A SPODIC HORIZON

Introduction

Oxalate significantly reduced P sorption capacity (Chapter 3). It has been observed that oxalate blocks sites on soil materials and thus reduces P sorption. Oxalate is continuously released into solution and competes with P for sorption sites. To understand the nature of competition between these two anions, it is important to study the influence of P on oxalate sorption capacity as well. The aim of this work was to investigate the sorption of oxalate in the presence of P as influenced by soil organic matter.

Materials and Methods

Soil Material

Soil was collected from the spodic horizon (Bh) in a single soil pit of a Pomona series (sandy, siliceous, hyperthermic Ultic Alaquod) at the Gator Nationals Forest site located in Alachua County, 10 km northeast of Gainesville, Florida (Swindel *et al.*, 1988). The soil material was air dried, passed through 2-

mm sieve, and stored in plastic bags. Samples preparation for the sorption studies was described in detail in chapter 2.

Sorption of Oxalate and Phosphate Added as a Mixture

Sorption experiments were carried out at different oxalate to phosphate molar ratios. The concentration of oxalate used was 1.0 mM, with a phosphate concentration of 0 mM, 0.1 mM, 1.0 mM, or 10 mM for the clay samples. Triplicate samples consisting of 250 mg of clay (with and without organic matter) were placed in 30 ml bottles along with 25 ml of solution. For the whole-soil samples, both with and without organic matter, an oxalate concentration of 1.0 mM was used along with phosphate concentrations of 0 mM, 0.1 mM, 0.5 mM, 1.0 mM, 3.0 mM, 7.0 mM or 10 mM. Triplicate five-gram samples of whole-soil from each treatment (with or without organic matter) were placed in 100 ml bottles along with 50 ml of solution. pH of the clay suspension and whole-soil was adjusted initially to 4.5, using 0.1 M HCl or NaOH.

Two drops of toluene were added to inhibit microbial growth and samples were placed in a reciprocating shaker for 24 hrs. The pH of the suspension was periodically (every three hours) adjusted with 0.1 M HCl or NaOH over the 24 hrs of the experiment, to maintain the initial pH. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. The filtrate was used for analysis of oxalate. Sorbed oxalate was calculated from the difference between initial and final oxalate concentrations in solution.

Oxalate in the extract was determined by HPLC (Fox and Comerford, 1990a) using a Hamilton PRP-X300 150 x 4.1 mm organic acid column (Hamilton Co., Reno, Nevada), with a Gilson single piston high pressure pump along with a Pheodyne model 7125 injection valve fitted with a 20 μL injection loop. This HPLC system uses a Gilson Holochrom variable wavelength UV detector in conjunction with a Gilson computerized integrator. The eluent was 0.005 M H_2SO_4 at a flow rate of 2 mL min^{-1} . Oxalate concentration was calculated from the calibration curve obtained with standard solutions of 0.1 to 10 mM.

Statistical Analysis

Statistical differences in the sorption of oxalate in the presence of P were compared. Significance of the difference between two means were determined by a t-test (Snedecor and Cochran, 1980). Standard errors of means are given as well.

Results

Less oxalate was sorbed by the clay fractions and by the whole-soil samples at high P concentrations. To evaluate the ability of P to depress oxalate sorption when both P and oxalate were added together, the percent efficiency of P in reducing the oxalate sorption was calculated according to the expression of Deb and Datta (1967):

$$P_e = 1 - \frac{Ox_p}{Ox_o} \times 100 \quad (\text{B-1})$$

where P_e is efficiency of P to reduce oxalate sorption (%), Ox_p is oxalate sorbed in the presence of P; and Ox_o is oxalate sorbed alone. Efficiency of phosphate in reducing the sorption of oxalate in the P + oxalate system for the clay fractions is presented in Table B-1. P was more effective in reducing oxalate sorption onto the clay fraction when organic matter was not present.

Table B-1. Percent reduction in oxalate sorption for the whole-soil samples and clay fractions (Mean \pm SD. n=3).

P:Oxalate molar ratio	Percent reduction in oxalate sorption	
	+ OM	- OM
Whole-Soil		
10:1	23.5 \pm 1.2 ^{aa}	18.5 \pm 0.9 ^{ab}
7:1	13.9 \pm 0.7 ^{ba}	12.3 \pm 0.7 ^{ba}
3:1	5.2 \pm 0.7 ^{ca}	5.5 \pm 0.4 ^{ca}
1:1	1.7 \pm 0.4 ^d	2.4 \pm 0.4 ^{da}
0.5:1	0.2 \pm 1.0 ^{da}	1.5 \pm 0.5 ^{da}
0.1:1	-0.9 \pm 0.8 ^{da}	1.6 \pm 0.3 ^{da}
Clay Fractions		
10:1	23 \pm 2 ^{aa}	56 \pm 2 ^{ab}
1:1	10 \pm 1 ^{ba}	28 \pm 4 ^{bb}
0.1:1	2 \pm 2 ^{ca}	1 \pm 1 ^{ca}

In each superscript first letter indicates significance among means within the column and second letter indicates significance among the rows, within the clay fraction and the whole-soil samples.

APPENDIX C

MEASUREMENT OF P DESORPTION FROM A SPODIC HORIZON USING DIFFERENT METHODS AT CONSTANT AND VARIABLE pH

Introduction

Inorganic soil P can be present in one of three different fractions: P in the soil solution; P on the mineral surfaces in the labile pool; or P in the nonlabile pool. The relationship between sorbed and solution P is often described by adsorption/desorption isotherms. Adsorption and desorption commonly exhibit hysteresis phenomena. Raven and Hossner (1993) showed a steeper isotherm slope for sorption than for desorption. To predict P uptake by plants, however, desorption isotherms are more useful since they evaluate the release of P into soil solution. The availability of P is often controlled by the desorption isotherm as a plant progressively extracts P from the soil around its roots (Yang *et al.*, 1991; Abrams and Jarrell, 1992; Graetz and Nair 1994; Harris *et al.*, 1994; Raven and Hossner, 1994). The desorption of soil P is a function of various soil parameters mainly: a) the concentration of sorbed P; b) the concentration of P in the soil solution; and c) the rate of P desorption into solution.

Spodic horizons can contain high amounts of amorphous Al oxides, which can sorb P. Some of the sorbed P is in a form unavailable to plants (Ballard and

Fiskell, 1974). While relatively large amounts of total P can be present in spodic horizons, water-soluble P tends to be low. According to Hingston *et al.* (1974), chemisorption and bi- and multidentate complex formation can decrease P desorption by increasing the irreversibility of sorbed P. Van Rees and Comerford (1986) observed that roots are present in the spodic horizon, and Neary *et al.* (1990), using a mechanistic nutrient uptake model, suggested that subsurface horizons could contribute a significant amount of the P required by southern pine. Soil buffering capacity used in this model was calculated using a sorption isotherm. To predict P uptake accurately, it may be important instead to determine and work with the P desorption isotherm.

Desorption of P is generally determined by one of three different methods: i) sequential extraction of soil with CaCl_2 , $\text{Ca}(\text{NO}_3)_2$ or other salt solution at a constant soil to solution ratio for a constant equilibration time; ii) equilibration of soil with $\text{Ca}(\text{NO}_3)_2$ or other salt solution at different soil-to-solution ratio for a constant time period; and iii) anion exchange-resin extraction, in which the soil is treated with different amounts of anion exchange resin in water or salt solutions for a constant time period. The first two methods study the chemical release of P from soil relating to the movement of P in the soil profile including plant uptake. The third method is more related to the overall extraction of P by plant roots. The anion-exchange resin instead proved inadequate for precise characterization of labile P, because it did not account for rate phenomena (Yang *et al.*, 1991; Abrams and Jarrell, 1992). This is because three steps are involved during

removal of P by anion exchange resin; i) release from the soil; ii) transport through the soil solution; and iii) sorption by the resin. In a recent study of P desorption in the field by Cooperband and Logan (1994) with an anion exchange membrane (AEM), it was shown that the AEM measured the net change and not the total change in P for the time period during which the resin is in contact with the soil. They stated that P was continuously adsorbed and desorbed from the membrane surface as a function of the soil chemical-biological microenvironment.

Soil pH has a strong effect on P sorption and desorption (Barrow, 1983) and P desorption leads in turn to a decrease in soil pH. Small differences in pH can have a significant influence on the P species present in solution. An equilibrium between the particular P species in solution and solid phase P controls the quantity of phosphate desorbed into solution. In most of the studies relating to P desorption, pH was not measured nor maintained constant (Logan, 1982; Menon *et al.*, 1989; Graetz and Nair 1994; Harris *et al.*, 1994; Raven and Hossner, 1994).

The objectives of this investigation were to: i) compare the P desorption isotherm obtained by a sequential extraction technique with that by a dilution method; and ii) compare P desorption under both constant and variable pH conditions by both methods.

Materials and Methods

Soil Material

Soil was collected from the spodic horizon (Bh) in a single soil pit of a Pomona series (sandy, siliceous, hyperthermic Ultic Alaquod) at the Gator Nationals Forest site located in Alachua County, 10 km northeast of Gainesville, Florida (Swindel *et al.*, 1988). The material was air dried, passed through a 2-mm sieve, and stored in plastic bags.

Preparation of Phosphorus Enriched Soil Material

Soil was enriched with 1000 ppm solution of P as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and incubated for 7 days at room temperature. At the end of this reaction period, samples were centrifuged, the soil samples were oven dried to constant weight at 110 °C, and the supernatant was analyzed for inorganic P. The difference between the amount of P added in the beginning and the amount of P in solution at the end of the reaction period was taken as the amount of P sorbed by the soil.

Desorption by a Dilution Method

This experiment was conducted both under constant and variable pH conditions. For one set of samples pH was kept constant, while for the other pH was allowed to change. For each set, a varying amount of a 0.01M calcium nitrate solution was added to three replicates of 5 gram soil samples. The soil to solution ratios used were 1:10, 1:20, 1:30, 1:40, 1:50, 1:75, and 1:100. Two

drops of toluene were added to inhibit microbial growth, and samples were placed in a reciprocating shaker for 24 hrs. For variable pH conditions, pH was measured at the begining and at the end of the reaction period. For constant pH conditions, pH of the suspension was periodically (every six hours) adjusted with 0.1 M HCl or NaOH over the entire period of time, to the initial pH value. At the end of the reaction period, each suspension was centrifuged at 12,000 g for 20 minutes. The supernatant solutions were analyzed for inorganic P and aluminum.

Desorption by a Sequential Extraction Method

Five grams of soil were repeatedly desorbed by 50 ml of 0.01 M calcium nitrate added in successive 24 hr periods for 8 days. The other experimental conditions were the same as described above, for the dilution method. The P concentrations in successive volumes were measured, and the total P desorbed from the soil was calculated by summation.

Chemical Analysis

Solution pH was measured using a combination glass electrode in conjunction with an Orion pH meter. Inorganic P in the filtrate was determined by a molybdenum-blue colorimetric procedure, using ascorbic acid as a reductant (Murphy and Riley, 1962).

Adsorption Isotherms

The Freundlich model was fitted to the desorption data. The Freundlich model has been found to be useful in describing desorption of ions into solution from soil particles (Sposito, 1984). The following equation was used:

$$S = K[C]^{\frac{1}{b}} \quad (C-1)$$

where S is the amount of P retained per unit mass of soil (mM kg^{-1}), C is the equilibrium concentration of P (mM), and K and b are empirical constants for the model. K and b were calculated by a least squares fit to a linear form of the Freundlich equation.

$$\log S = \log K + \frac{1}{b} \log C \quad (C-2)$$

The derivative of this function with respect to C equals the K_d (solid to solution partition coefficient) value which can be expressed by:

$$K_d = \frac{K}{b} \times [C]^{\frac{1}{b}-1} \quad (C-3)$$

where K and b are the empirical constants calculated from the Freundlich equation.

Statistical Analysis

The linearized form of the Freundlich equation was used to test the statistical differences between different regression lines using the General Linear

Models procedure in the SAS framework (SAS Institute, 1985). The model used was:

$$Y_{ij} = \alpha + \beta X_{ij} + \epsilon_{ij} \quad (C-4)$$

where α is the intercept, β is the slope of the line and ϵ is the error term. To compare two regression lines, we have compared the β_1 and β_2 values of the two lines. The ANOVA and t tests were used to test the difference between α_1 and α_2 , and between β_1 and β_2 .

Results

Desorption Isotherms

The desorption isotherms obtained by dilution and sequential extraction methods under conditions of constant and variable pH are presented in Figure C-1. Desorption isotherms followed the Freundlich model. With parameters of the isotherms as given in Table C-1. The slopes of the regression lines for the different methods illustrate that the change in surface-sorbed P relative to solution P were significantly different for the two methods. The variable vs constant pH approaches did not significantly influence the amount of P released. The dilution method, both at variable and constant pH, had a statistically lower release of P into solution compared to the sequential extraction method at the same level of P present on soil surfaces.

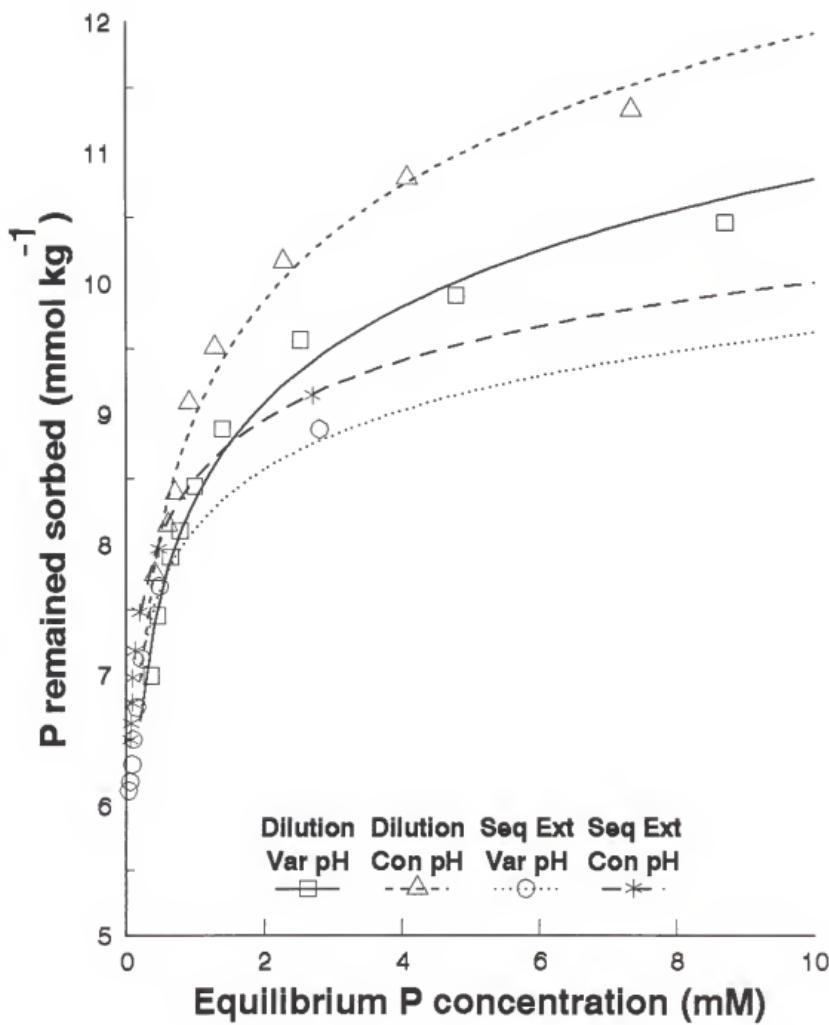


Fig. C-1. P desorption curves by dilution and extraction methods at both variable and constant pH.

Table C-1 Freundlich isotherm parameters for the desorption of P from soil using the dilution and sequential extraction methods at variable and constant pH.

Desorption Method	pH Conditions	Parameters of the Freundlich isotherm		
		Slope	Intercept	R ²
Dilution	Constant	0.121 ^a	2.20 ^a	0.96
	Variable	0.114 ^a	2.12 ^b	0.94
Sequential	Constant	0.088 ^b	2.08 ^b	0.95
	Variable	0.083 ^b	2.14 ^b	0.94
Dilution [@]		0.117 ^a	2.16 ^a	0.99
Sequential [@]		0.086 ^b	2.11 ^b	0.98

@Includes all samples at variable and constant pH

Values within columns for different methods followed by the same letter are not significantly different at the 5 % level.

Using the Freundlich isotherms, the partition coefficients (K_d) also were calculated. The plot of K_d vs solution P is presented in Fig C-2. The results of this study show that the two desorption methods differed significantly. The amount of P desorbed by the dilution method under constant and variable pH was less than for the sequential method. This resulted in higher partition coefficient (K_d) values for P being calculated by the dilution method.

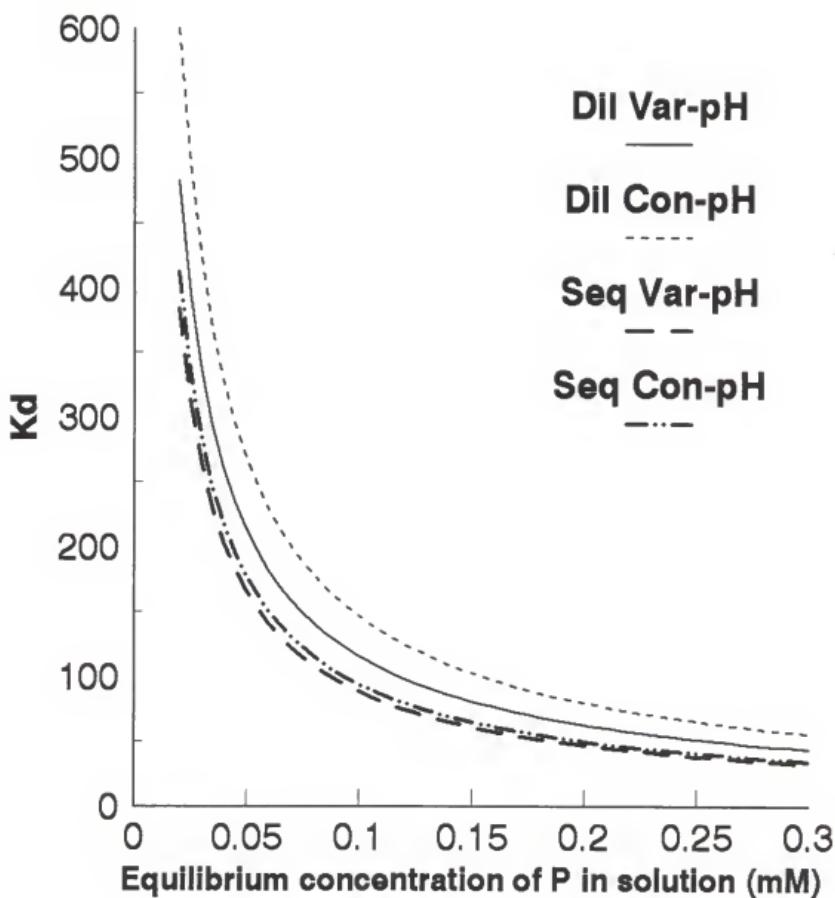


Fig. C-2. Relationship between K_d and the equilibrium concentration of P as obtained by different methods.

APPENDIX D
DESORPTION OF P AND OXALATE

Table D-1 Influence of previously sorbed P by clay and whole-soil samples on oxalate sorption and release of P, Al, Fe, OH, and organic carbon (Mean \pm SD, n = 3).

P Previously Present (mmol kg ⁻¹)	Oxalate Sorbed (mmol kg ⁻¹)	Amount Released (mmol kg ⁻¹)				OC [^] (mg g ⁻¹)
Clay without Organic Matter						
545 \pm 9	175 \pm 7	70.1 \pm 1	188 \pm 5	2.6 \pm 0.07	326 \pm 11	
91 \pm 0.3	191 \pm 1	25.5 \pm 1	186 \pm 4	2.7 \pm 0.07	364 \pm 18	
9.5 \pm 0.5	205 \pm 6	4.3 \pm 1	185 \pm 1	2.9 \pm 0.09	390 \pm 14	
Clay with Organic Matter						
353 \pm 5	205 \pm 4	49 \pm 0.5	225 \pm 1	2.5 \pm 0.15	344 \pm 14	267 \pm 6
72 \pm 0.7	204 \pm 2	18 \pm 0.1	225 \pm 2	2.9 \pm 0.07	381 \pm 7	277 \pm 7
9.2 \pm 0.8	227 \pm 3	5 \pm 0.1	230 \pm 3	3.1 \pm 0.03	415 \pm 9	267 \pm 6
Soil without Organic Matter						
24.5 \pm 0.7	9.4 \pm 0.3	9.7 \pm 0.1	4.8 \pm 0.1	0.12 \pm 0.01	15 \pm 1	
21.7 \pm 0.6	10.5 \pm 0.2	7.4 \pm 0.1	4.2 \pm 0.1	0.11 \pm 0.01	18 \pm 1	
16.2 \pm 0.2	10.7 \pm 0.1	2.5 \pm 0.1	4.0 \pm 0.1	0.12 \pm 0.01	18 \pm 1	
7.1 \pm 0.1	12.1 \pm 0.6	1.5 \pm 0.1	3.9 \pm 0.1	0.11 \pm 0.01	20 \pm 2	
3.7 \pm 0.1	12.4 \pm 0.1	0.9 \pm 0.1	4.1 \pm 0.1	0.09 \pm 0.00	22 \pm 1	
0.8 \pm 0.1	12.5 \pm 0.4	0.5 \pm 0.1	4.4 \pm 0.1	0.11 \pm 0.01	25 \pm 2	
Soil With Organic Matter						
16.7 \pm 0.5	2.4 \pm 0.1	9.2 \pm 0.2	27 \pm 1	0.13 \pm 0.01	4.2 \pm 0.2	3.4 \pm 0.1
15.5 \pm 1.4	2.7 \pm 0.1	7.8 \pm 0.1	35 \pm 1	0.14 \pm 0.01	4.8 \pm 0.2	3.8 \pm 0.1
10.2 \pm 0.7	2.8 \pm 0.3	4.6 \pm 0.1	35 \pm 1	0.15 \pm 0.01	5.2 \pm 0.7	3.9 \pm 0.1
5.4 \pm 0.2	5.9 \pm 0.4	2.3 \pm 0.1	36 \pm 1	0.17 \pm 0.01	10.5 \pm 0.2	4.9 \pm 0.1
4.1 \pm 0.1	6.8 \pm 0.5	1.1 \pm 0.1	37 \pm 1	0.17 \pm 0.01	12.7 \pm 0.9	4.4 \pm 0.1
0.9 \pm 0.1	6.9 \pm 0.3	0.6 \pm 0.1	37 \pm 1	0.19 \pm 0.01	12.7 \pm 0.2	4.5 \pm 0.1

[^] OC = Organic carbon.

Table D-2 Influence of oxalate previously present on P sorption and release of oxalate, Al, Fe, OH, and organic carbon by clay fractions and whole-soil samples (Mean \pm SD, n = 3).

Oxalate Previously Present (mmol kg ⁻¹)	P Sorbed (mmol kg ⁻¹)	Ox	Amount Released (mmol kg ⁻¹)			OC [^] (mg g ⁻¹)
			Al	Fe	OH	
Clay without Organic Matter						
456 \pm 17	271 \pm 1	29.3 \pm 0.5	36 \pm 1	0.05 \pm 0.02	256 \pm 6	
48 \pm 2.4	283 \pm 1	9.2 \pm 0.4	33 \pm 0	0.01 \pm 0.01	286 \pm 13	
2.7 \pm 0.5	305 \pm 1	1.1 \pm 0.2	21 \pm 1	0.08 \pm 0.0	300 \pm 20	
Clay with Organic Matter						
275 \pm 14	119 \pm 2	0.49 \pm 0.02	21 \pm 0.8	0.81 \pm 0.03	107 \pm 5	21 \pm 1
43 \pm 0.2	179 \pm 3	0.24 \pm 0.1	8 \pm 0.5	0.21 \pm 0.03	175 \pm 18	46 \pm 1
4.8 \pm 0.2	98 \pm 4	0.09 \pm 0.06	8 \pm 0.5	0.15 \pm 0.02	188 \pm 7	46 \pm 1
Soil Without Organic matter						
14.9 \pm 0.7	8.3 \pm 0.1	1.1 \pm 0.06	3.4 \pm 0.1	0.03 \pm 0.01	9.0 \pm 1	
12.4 \pm 0.4	9.2 \pm 0.2	0.2 \pm 0.01	2.1 \pm 0.1	0.03 \pm 0.01	9.3 \pm 1	
9.6 \pm 0.5	10.8 \pm 0.3	0.2 \pm 0.01	1.7 \pm 0.1	0.03 \pm 0.01	12.5 \pm 2	
6.2 \pm 0.7	12.9 \pm 0.1	0.2 \pm 0.01	1.5 \pm 0.1	0.04 \pm 0.01	12.5 \pm 2	
4.0 \pm 0.1	13.8 \pm 0.1	0.1 \pm 0.01	1.6 \pm 0.1	0.02 \pm 0.01	11.7 \pm 1	
0.8 \pm 0.1	14.1 \pm 0.1	0.1 \pm 0.01	1.1 \pm 0.1	0.01 \pm 0.01	14.1 \pm 2	
Soil With Organic Matter						
11.6 \pm 1.0	5.7 \pm 0.1	1.9 \pm 0.1	4.6 \pm 0.1	0.06 \pm 0.01	5.9 \pm 1	1.1 \pm 0.1
8.8 \pm 0.6	7.8 \pm 0.2	0.9 \pm 0.1	4.1 \pm 0.1	0.04 \pm 0.01	8.6 \pm 2	1.0 \pm 0.1
7.4 \pm 0.1	9.1 \pm 0.4	0.2 \pm 0.1	1.6 \pm 0.1	0.02 \pm 0.01	9.6 \pm 1	0.8 \pm 0.0
5.5 \pm 0.2	10.3 \pm 0.8	traces	1.4 \pm 0.1	0.01 \pm 0.01	11.1 \pm 1	0.7 \pm 0.1
4.0 \pm 0.1	10.9 \pm 0.3	traces	1.2 \pm 0.1	0.01 \pm 0.01	10.6 \pm 1	0.7 \pm 0.1
0.8 \pm 0.1	10.9 \pm 0.1	traces	0.7 \pm 0.1	0.01 \pm 0.01	11.4 \pm 1	0.6 \pm 0.1

[^] OC = Organic Carbon.

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BIOGRAPHICAL SKETCH

Jagtar Singh Bhatti was born on March 9, 1958 in Jalandhar, Punjab, India. He attended high school in Ludhiana and graduated from Malwa Khalsa High School in 1974. He went to Punjab Agricultural University Ludhiana, Punjab and received his Bachelor of Science (1979) and Master of Science in Soil Science (1981). He joined the faculty of Soil Science at Punjab Agricultural University Ludhiana, Punjab and taught undergraduate courses in soil science. In December 1984, he met Gurmeet and got married. In June 1985, they decided to migrate to Canada. After coming to the cold country, Jagar entered another Master's program in soil chemistry at University of Saskatchewan, Saskatoon and graduated in 1988. Jagtar worked as Research Assistant at University of Washington, Seattle for one and a half years. After traveling into Far Eastern countries and Australia for about four months, in May 1991, he joined University of Florida for Doctor of Philosophy in Forest Soils in the Department of Soil and Water Science. He is currently employed as an Ecological Modeler at Sault Ste. Marie, Ontario, Canada for Forestry Canada Ontario Region.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy

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Professor of Soil and Water Science

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Earl L. Stone
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Professor of Soil and Water Science

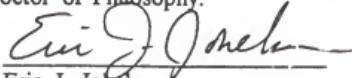
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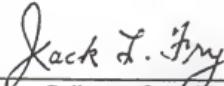


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This dissertation was submitted to the Graduate Faculty of the College of Agriculture and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1995



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